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GAS TURBINE AND JET ENGINE FUELS

SUMMARY REPORT

NAVY BUWEPS CONTRACT N600(19)-58219

MARCH, 1963

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PHILLIPS PETROLEUM COMPANY

PHILLIPS PETROLEUM COMPANY
RESEARCH DIVISION
BARTLESVILLE, OKLAHOMA

SUMMARY REPORT

Navy BuWeps Contract N600(19)-58219

GAS TURBINE AND JET ENGINE FUELS

By

W. L. Streets

R. M. Schirmer

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S U M M A R Y

This report summarizes results of jet fuel performance studies carried out by Phillips Petroleum Company under Navy Bureau of Weapons Contract N600(19)-58219 during the twelve month period between April 1, 1962 and March 31, 1963. The primary effort under this contract has been evaluation of the effects of fuel sulfur and ingested sea water on hot gas corrosion of turbine inlet guide vanes using specimens fabricated from five typical current-generation alloys including Udimet 500, Waspalloy, Rene' 41, Hastelloy R-235 and Haynes Alloy 25. A second project consisted of a study of test methods for evaluating the burning quality of jet fuels.

Twelve-hour duration tests conducted with the Phillips 2-Inch Research Combustor operated at a pressure of 12 atmospheres and 2000F exhaust gas temperature showed that: (1) guide vane metal loss is approximately a linear function of time; (2) a fuel sulfur content of 1.0 per cent had no detrimental effect on the rate of metal loss; (3) only one of the five alloys tested, Haynes Alloy 25, exhibited significantly more loss in tensile strength with sulfur than without; (4) all alloys suffered marked losses in ductility, though no sulfur effect was indicated; (5) photomicrographs suggested predominantly intergranular attack, which was not increased by the addition of sulfur to the fuel.

A brief feasibility study of the potential usefulness of the Phillips Microburner to supplement the 2-inch combustor and eventually provide a means for more rapid evaluation of fuel and air contaminants was encouraging. Further work may be justified to establish whether a useful correlation of metal loss data exists between the atmospheric pressure Microburner and high pressure combustors.

(Continued)

JUL 26 1963

S U M M A R Y (Cont'd)

A bench-scale study of sulfur corrosion of the type known colloquially as "black plague" was also conducted using a semi-dynamic furnace test procedure. The same five alloys evaluated in the 2-inch combustor were studied in this program. These tests were carried out at 2000 F with various combinations of air, sulfur dioxide, carbon and sea salts present. The objectives were to reproduce the type of attack reported by other investigators and to assess the relative importance of the several factors postulated as responsible for the attack. Others have attributed this attack to unburned carbon, ingested sea salts and/or fuel sulfur. The results of this program indicate that: (1) "black plague" type attack was reproduced; (2) metal loss was not a wholly reliable index to degree of attack; (3) extent of attack was demonstrated to be potentially catastrophic; (4) of the individual corrodents, only sea salt increased the attack above the "air only" baseline; (5) the effect of sea salt alone and in combination with carbon and/or SO_2 was specific to alloy type (6) carbon, as a possible reducing agent for protective chromium oxide films, was confirmed as detrimental to all the alloys in tests with SO_2 and air; (7) carbon accelerated sea salt corrosion of three alloys and markedly inhibited sea salt corrosion of the other two alloys; (8) when sulfur was present as both sea salts and SO_2 (no carbon) results varied from mild acceleration by the added SO_2 to pronounced inhibition depending on alloy type; (9) when carbon was included while supplying both SO_2 and sea salts the attack was accelerated for all but one alloy, René 41, where, again, attack was apparently inhibited by the carbon and SO_2 ; (10) except for René 41 corrosion was catastrophic with air + carbon + SO_2 + sea salt; (11) checks for magnetic properties in scale removed from each test strip showed all were non-magnetic; (12) a number of test strips became strongly magnetic following exposure, suggesting some enrichment in nickel and/or cobalt by virtue of losses in the non-magnetic alloying metals.

In view of the suggestion of one engine manufacturer that fuel hydrogen content might be used as an index of fuel burning quality, hydrogen content was compared to Luminometer Number and Smoke Point as a function of flame radiation data in several combustors. The suitability of hydrogen content as a correlating parameter was confirmed. Hydrogen content unlike Luminometer Number and Smoke Point, reflects the similarity in combustor radiation data that exist between the normal and isoparaffins. A comparison of the test methods indicates that hydrogen content has an advantage with respect to repeatability and reproducibility.

SUMMARY REPORT
Navy BuWeps Contract N600(19)-58219
GAS TURBINE AND JET ENGINE FUELS

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PHILLIPS PETROLEUM COMPANY

BARTLESVILLE, OKLAHOMA

SUMMARY REPORT

Navy BuWeps Contract N600(19)-58219

GAS TURBINE AND JET ENGINE FUELS

I. INTRODUCTION

This report summarizes Navy sponsored jet fuel performance studies carried out by Phillips Petroleum Company under Contract N600(19)-58219 during the twelve month period between April 1, 1962 through March 31, 1963.

The primary effort during this contract has been to evaluate the effects of fuel sulfur and ingested sea water on hot gas corrosion of turbine inlet guide vanes. This work is a continuation of that originally begun under Contract Noas 58-310-d and continued under contracts Noas 60-6009-c and NO(w) 61-0590-d. Emphasis under the present contract has been placed on obtaining information on the durability of several typical current-generation superalloys in sulfurous and/or sea salt-laden atmospheres at 2000 F which is representative of maximum turbine inlet temperature in the most advanced design turbojet engines.

A second project has consisted of a study of test methods for evaluation of the burning qualities of jet fuels. A critical analysis of the present methods, Smoke Point and Luminometer Number, was made and the ratings of fuels by these methods correlated with measurements of their cleanliness in full-scale aircraft gas turbine combustors. Similar correlations of performance with fuel hydrogen contents were made which indicate that hydrogen content provides a superior measure of combustion cleanliness for jet fuels.

II. EFFECTS OF FUEL SULFUR CONTENT AND SEA WATER INGESTION
ON THE DURABILITY OF JET ENGINE "HOT SECTION" COMPONENTS

A. 2-Inch Combustor Turbine Inlet Guide Vane Durability Tests

1. Test Procedure and Equipment

The Phillips 2-inch Research Combustor illustrated in Figure 1 has been described in previous reports (1). Briefly, this is a 2-inch diameter axial flow combustor embodying the principal features of modern jet engine combustion systems. Air is supplied to the combustor from a compression and heating plant described in (1), while fuel is supplied to the swirl type nozzle by nitrogen pressurization. The design of the combustor provides for ready removal of flame tubes and turbine blading test pieces for weighing and inspection.

The test conditions employed were the same as those used for previous investigations of the effect of sulfur on flame tubes which have been reported in (2), (3), and (4). Combustor pressure was held at 350 inches mercury absolute, inlet air temperature at 700 F and inlet reference velocity at 100 fps, providing conditions which are reasonably realistic for high compression ratio turbojets operating at relatively low altitudes. Fuel air ratio was held at 0.020 pounds of fuel per pound of air which produced exhaust gas temperatures from 1950 to 2000 F, providing a severity level representative of maximum turbine inlet temperatures in the most advanced engine designs.

For investigation of metal loss from turbine blades no change was made to the combustor. The only change in apparatus was to add a six-inch spool piece downstream from the combustor and to cut a suitable cavity into its mating flange for the test piece holder shown in Figure 2, placing these pieces in a position comparable to blading in an actual engine.

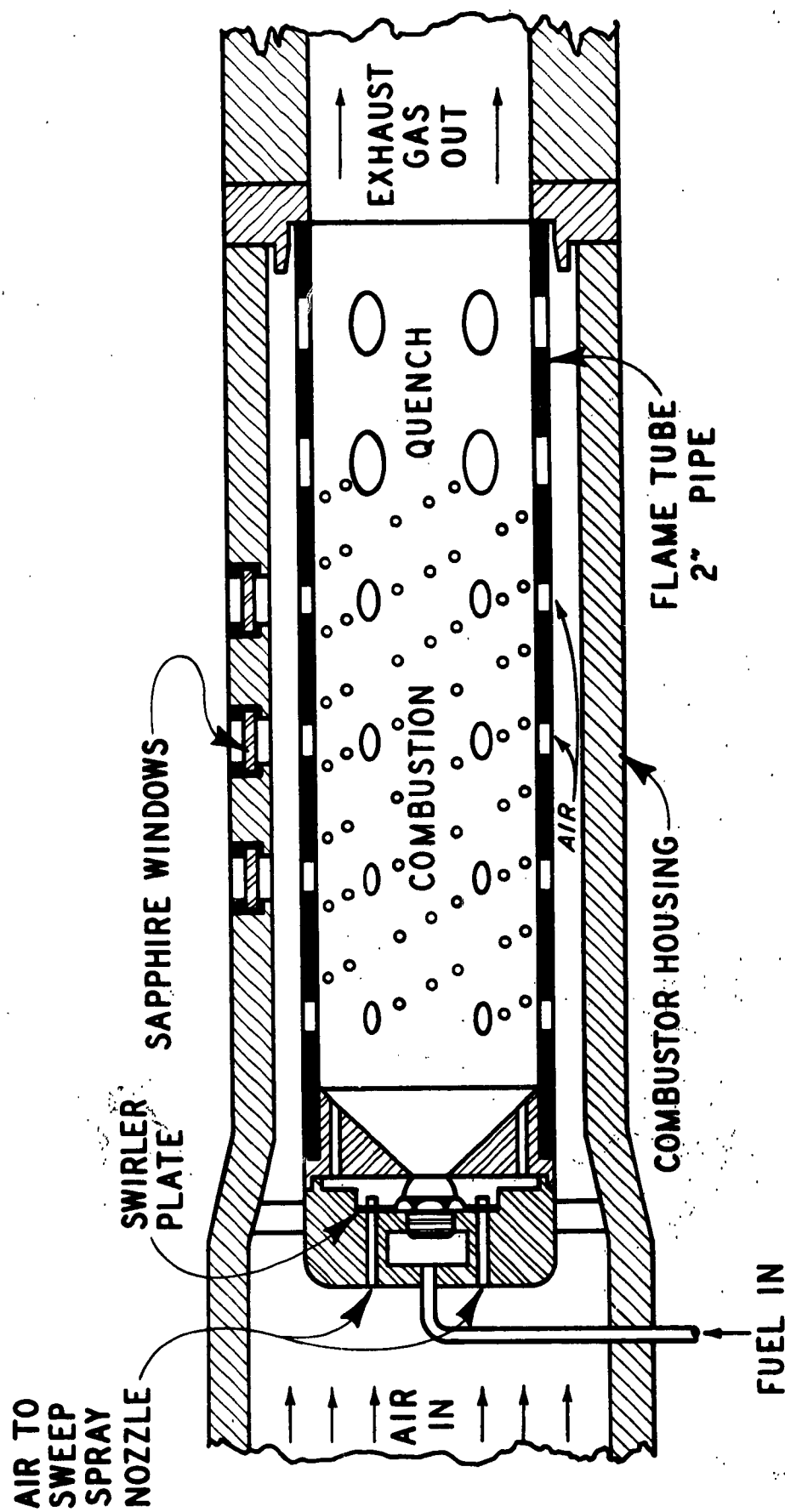


FIGURE 1

PHILLIPS LABORATORY SCALE TEST COMBUSTOR

HOLDER MAT'L: 310 SS; STRIP MAT'L.: VARIOUS TURBINE BLADING ALLOYS
 SCALE: 1" 1"

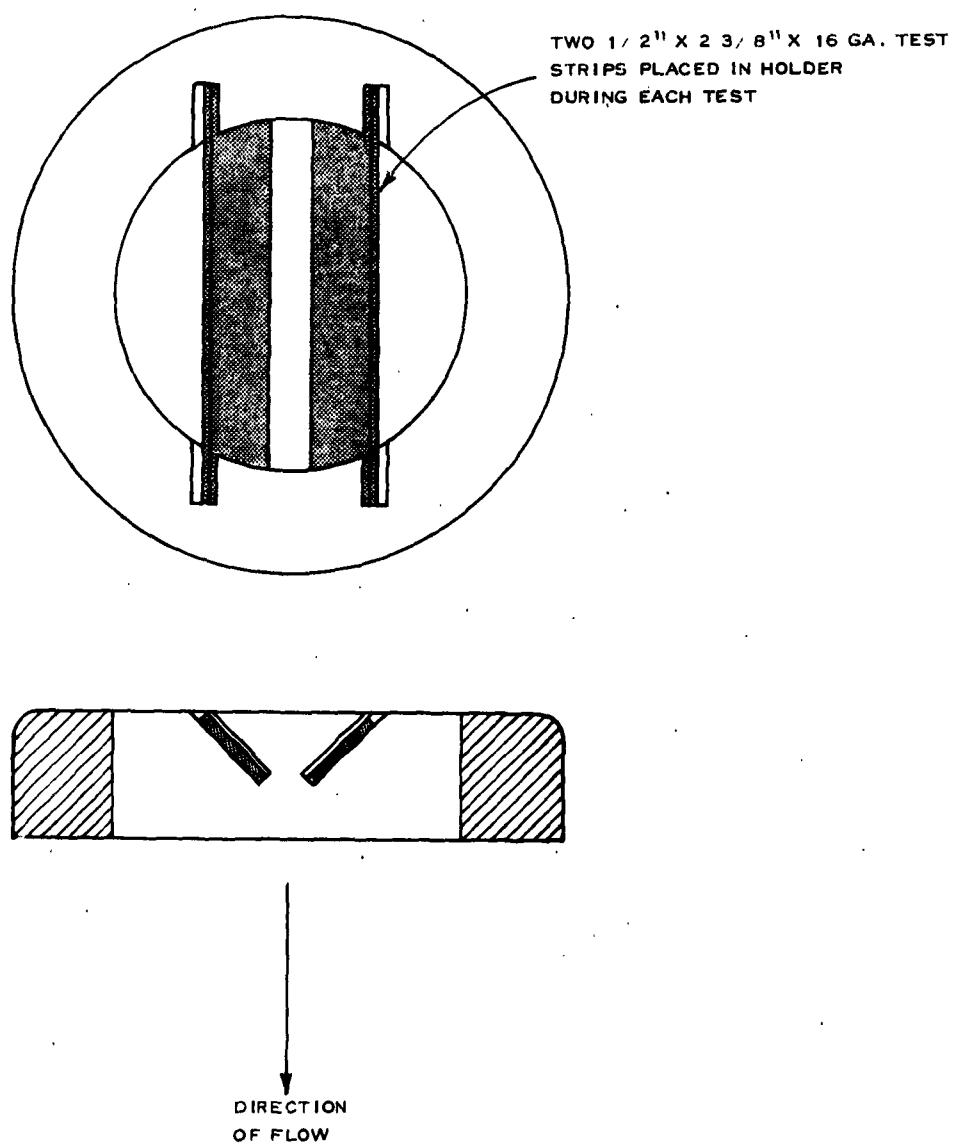


FIGURE 2
 SPECIMEN HOLDER FOR PHILLIPS 2-INCH COMBUSTOR SIMULATED
 TURBINE INLET GUIDE VANE DURABILITY TESTS

Earlier work reported in (4) was carried on using a cartwheel-shaped specimen to simulate guide vanes. Owing to the difficulties encountered in fabricating this shape from the relatively hard-to-work superalloys, a change in specimen configuration was adopted during this contract. The new specimens are simply 1/2" by 2 3/8" strips cut from 16 gauge sheet. Two of these strips are placed in the exhaust gas stream as shown in Figure 2.

The duration of exposure of the pair of specimens was 12 hours obtained by running six two-hour intervals, the specimens being descaled by rotary wire brushing at the end of each 2 hour period. The data are reported as milligrams of accumulated metal loss (both strips) per square centimeter of exposed area. During this contract vane pieces fabricated from Udimet 500, Waspalloy, Haynes Alloy 25, Hastelloy R-235 and Rene' 41 have been tested. The compositions of these alloys are shown in Table I. These materials are typical of current-generation superalloys of the type utilized in the fabrication of turbine inlet guide vanes.

Since previous investigations (3) had shown sulfur compound type to be unimportant as compared to gross sulfur content, it was decided to use only ditertiarybutyldisulfide as the sulfur contaminant since it is inexpensive and available at adequate purity. In order to exaggerate the sulfur severity for testing purposes this compound was added to the base fuel in sufficient concentration to realize 2.5 times the jet fuel specification sulfur limit of 0.4 per cent (wt.), or, in other words, 1.0 per cent sulfur.

The base fuel selected for this work, as in previous investigations, was a JP-5 type isoparaaffinic alkylate containing 0.005 per cent or less sulfur. Typical properties of this base fuel are shown in Table II.

TABLE I
COMPOSITION OF ALLOYS USED IN TURBINE GUIDE VANE METAL LOSS TESTS

Alloy	Per Cent by Weight of Indicated Metal																
	Cr	W	Fe	C	Si	Co	Ni	Mn	Cb	Mo	P	S	Al	Ti	B	Zr	Cu
Udimet 500 *	19.0	-	.36	.09	.15	18.7	51.04	<.10	-	4.35	-	.005	3.10	2.99	.003	<.01	<.10
Waspalloy*	19.5	-	.95	.053	.03	13.2	57.44	.01	-	4.41	.003	.003	1.23	3.10	.002	.06	.01
Haynes Alloy 25	20.0	15.0	3.0	.1	1.0	Bal.	10.0	1.5	-	-	-	-	-	-	-	-	-
Hastelloy R-235*	15.29	-	9.96	.15	.26	.38	63.91	.03	-	5.48	.001	.009	2.05	2.48	-	-	-
René 41*	18.33	-	1.90	.10	.16	10.69	54.37	.05	-	9.69	-	.009	1.54	3.15	.005	-	-

* Specific analyses for particular samples tested in combustor.. Values shown for other alloys are typical compositions.

TABLE II

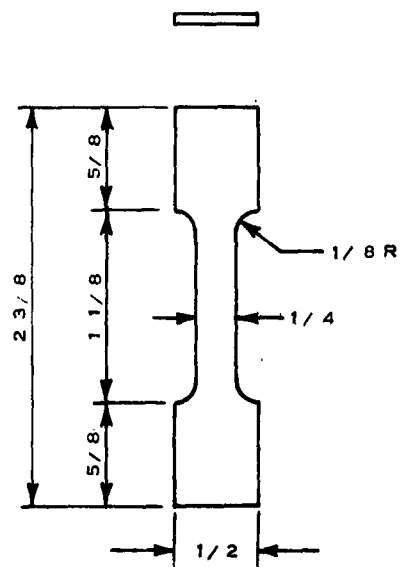
TYPICAL PROPERTIES OF JP-5 TYPE ISOPARAFFINIC BASE FUEL USED
IN TURBINE GUIDE VANE DURABILITY STUDIES

ASTM Distillation	
IBP, F	357
10% Evap.	367
50% Evap.	390
90% Evap.	472
EP	549
API Gravity	53.0
Bromine Number	1.4
Aniline Point, F	191.5
Copper Corrosion, 3 hrs. @ 212F	1
Flash Point, F	145
Doctor Test	Negative
Color, Saybolt	+30
Kinematic Viscosity, cs @ 32F	4.05
cs @ 100F	1.77
Sulfur Content, % wt., Total	0.005
Mercaptans	0.001
Composition, Vol. %	Essentially 100% Paraffins

The exposed specimens of each alloy were fabricated into the shape shown in Figure 3 and their tensile strength determined using an Instron Model TCC testing machine operated at a crosshead travel of 0.1 inch per minute. Gauge length was 1-inch. Tensile data were obtained on the unexposed metal samples and those exposed for 12 hours with the sulfur-free base fuel and with the 1 per cent sulfur-treated fuel. In addition to tensile data, photomicrographs were also obtained on the unexposed samples and on those exposed to the sulfur-free fuel and to the 1 per cent sulfur fuel. The photomicrographs were prepared both before and after etching of the metal samples.

2. Results and Discussion

The data obtained during this contract on the effect of fuel sulfur contamination on metal loss from Waspalloy, Udimet 500, Haynes Alloy 25, Rene' 41 and Hastelloy R-235 simulated turbine inlet guide vanes are shown in Figures 4 and 5. As mentioned previously these data were obtained at a nominal exhaust gas temperature of 2000F for a test duration of 12 hours. Originally it was intended only to run these tests for a duration of 6 hours. However, as will be pointed out later, with reference to the Phillips Microburner test, there were some indications that this test duration should be extended in order to be assured of a sufficient test duration to accurately develop the trend of sulfur effect. With the exception of Udimet 500, the 12 hour extended tests were conducted using the original specimens from the six hour tests reported in (6). This was also attempted with Udimet 500 strips but malfunction of the propane igniter system caused flame impingement on the specimens, resulting in their destruction. Therefore it was necessary to restart the Udimet 500 test with new strips.



NOTE: TENSILE SPECIMENS TO BE FABRICATED FROM $\frac{1}{2} \times 2 \frac{3}{8} \times 16$ GAGE
NEW AND EXPOSED CORROSION TEST STRIPS FROM 2-INCH COMBUSTOR TESTS.

FIGURE 3
TENSILE TEST CONFIGURATION FOR TURBINE INLET GUIDE VANE
CORROSION SPECIMENS

Figure 4 indicates that no marked acceleration of metal loss rate was observed between 6 and 12 hours either with or without sulfur in the fuel. In addition, extension of the test duration did not alter the relative rankings of the alloys appreciably.

It will be observed from Figure 5 that 1 per cent sulfur in the isoparaffinic base fuel had either no effect or an apparent beneficial effect on the durability of this group of superalloys. A statistical analysis of variance was performed on these data. This analysis resulted in acceptance of the null hypothesis; that is, that there is no difference between the means of the two fuels (base and base + 1 per cent sulfur). These tests suggest that 1 per cent sulfur is neither beneficial nor detrimental from the standpoint of turbine inlet guide vane metal loss. However, the analysis of these data in terms of alloy effects resulted in a rejection of the null hypothesis; that is, a significant difference among means of the different metals is indicated. The results of the analysis of variance are shown in Appendix I.

Considering the results shown in Figure 5 in terms of the relative durability of the several alloys, it will be noted that the extremes are Haynes Alloy 25 (lowest loss) and Hastelloy R-235 (highest loss). These extremes differ by a factor of about five while the balance of the alloys lie intermediate and differ from each other by values believed to lie within the repeatability of the test method and apparatus.

The data obtained on tensile strengths after 12 hours exposure to a sulfur-free and a sulfurous atmosphere are shown in Table III and Figures 6, 7, 8, 9 and 10. As indicated, only two of the alloys, Waspalloy and Haynes Alloy 25, showed more degradation of tensile strength by the addition of 1.0 per cent sulfur to the fuel than was observed with the sulfur-free fuel. Of these two materials, the effect of sulfur was by far the

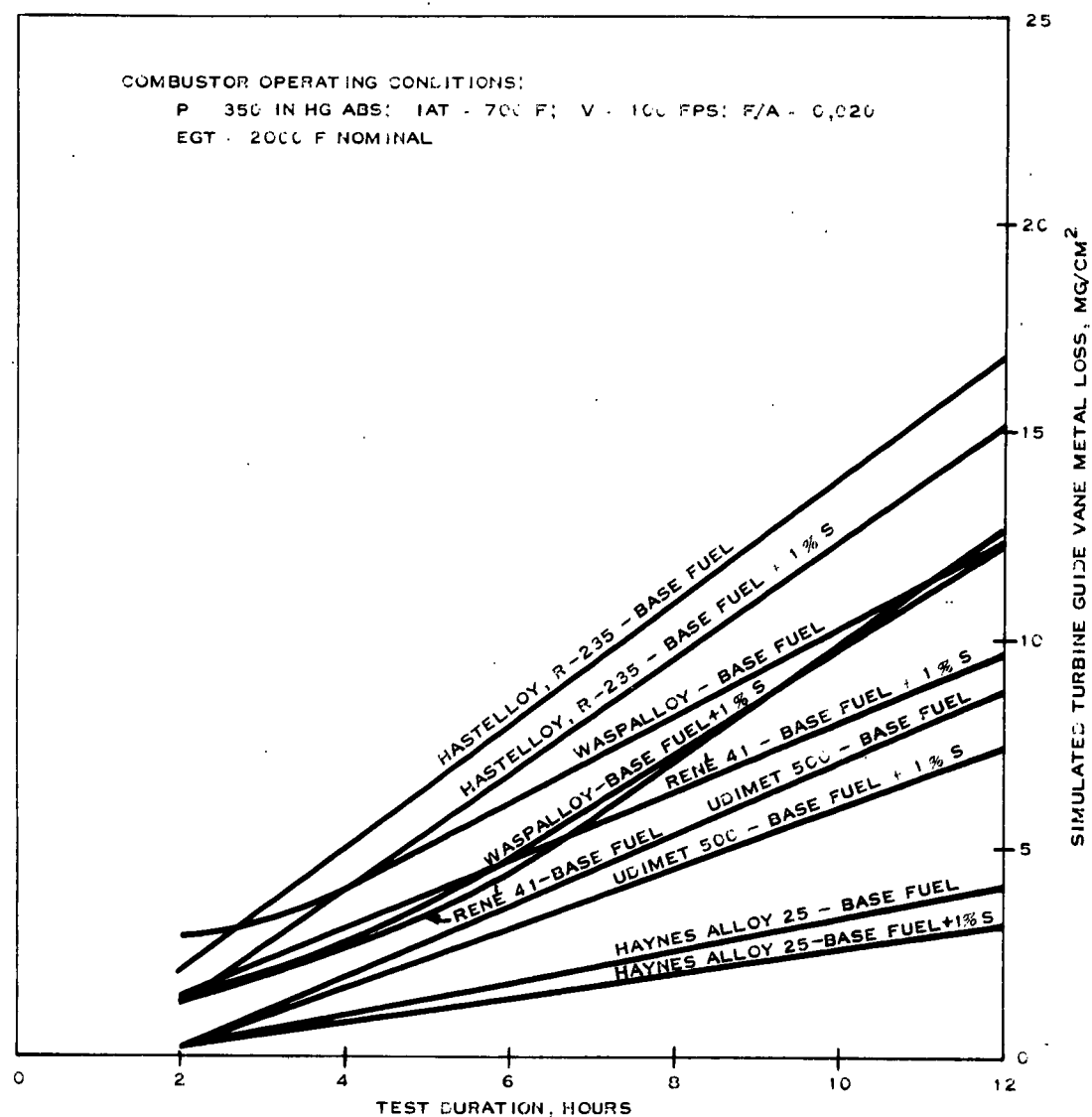


FIGURE 4
TURBINE GUIDE VANE METAL LOSS AS A FUNCTION OF TEST DURATION

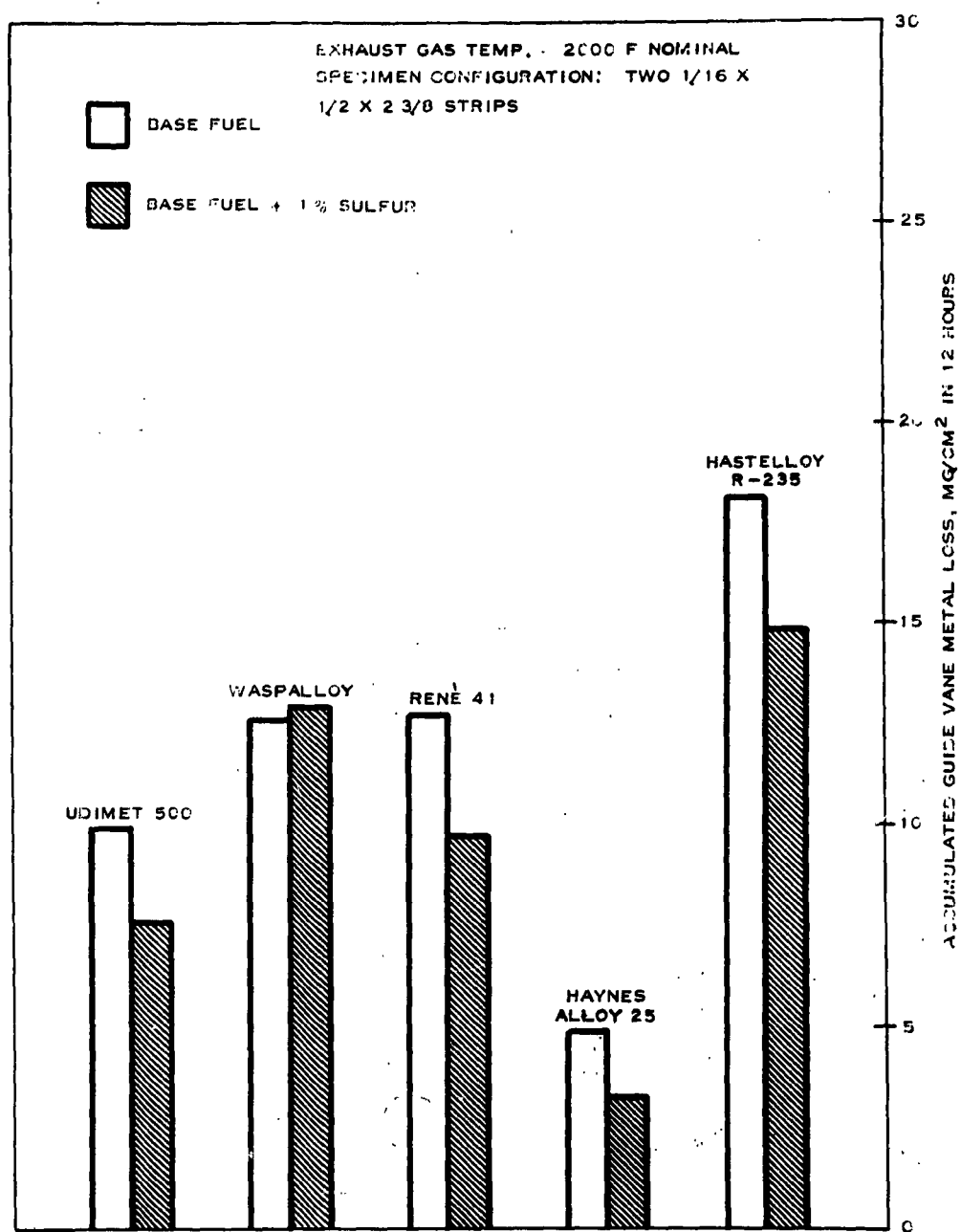


FIGURE 5
EFFECT OF FUEL SULFUR CONTAMINATION ON TURBINE GUIDE
VANE METAL LOSS FROM SEVERAL SUPERALLOYS IN THE PHILLIPS 2-INCH COMBUSTOR

TABLE III
EFFECT OF TWELVE HOURS EXPOSURE TO SULFUR-FREE AND SULFUROUS EXHAUST
GASES ON THE TENSILE STRENGTH OF FIVE SUPERALLOYS

Alloy	Tensile Strength Before Exposure, psi	Tensile Strength After 12 Hour Exposure at 2000F w/Base Fuel, psi	Tensile Strength After 12 Hour Exposure at 2000F w/Base Fuel + 1% Sulfur, psi	Change in Tensile Strength After Exposure to Sulfur-Free Exhaust Gases, psi	Change in Tensile Strength After Exposure to Sulfurous Exhaust Gases, psi
Udimet 500	156,380	125,425	133,930	-30,955	-22,450
Waspalloy	120,650	124,415	111,530	+ 3,765*	- 9,120
Rene' 41	136,000	119,400	120,760	-16,600	-15,240
Haynes Alloy 25	146,750	126,670	107,470	-20,080	-39,280
Hastelloy R-235	130,300	125,470	133,090	- 4,830*	+ 2,790*

* These changes are insignificant since they are less than the least significant difference (95 per cent confidence) of 5,750 psi calculated from data on the unexposed specimens..

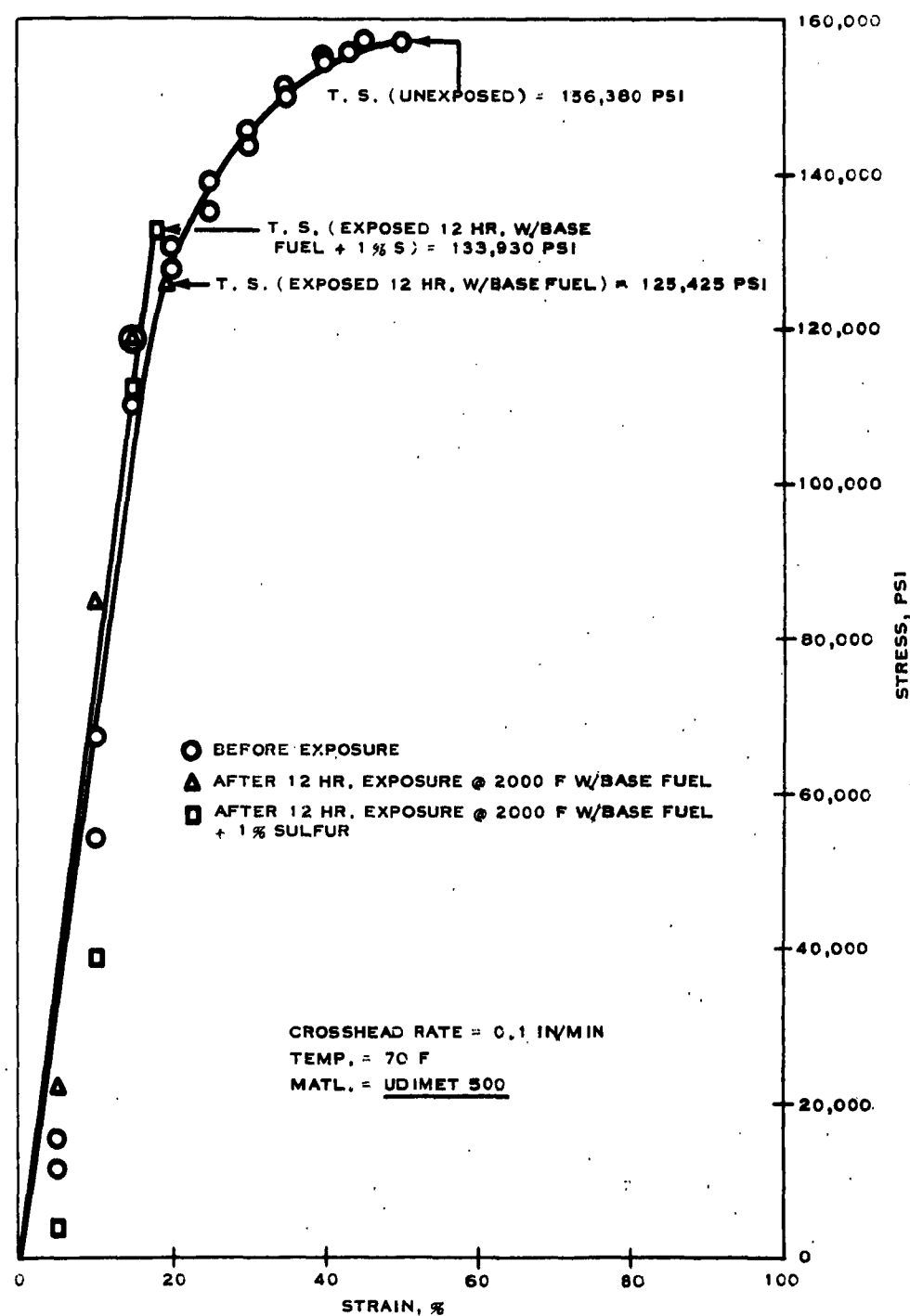


FIGURE 6
STRESS-STRAIN CURVE FOR UDIMET 500 BEFORE AND AFTER
12 HOURS EXPOSURE TO SULFUR-FREE AND SULFUROUS EXHAUST GAS @ 2000 F
IN THE PHILLIPS 2-INCH RESEARCH COMBUSTOR

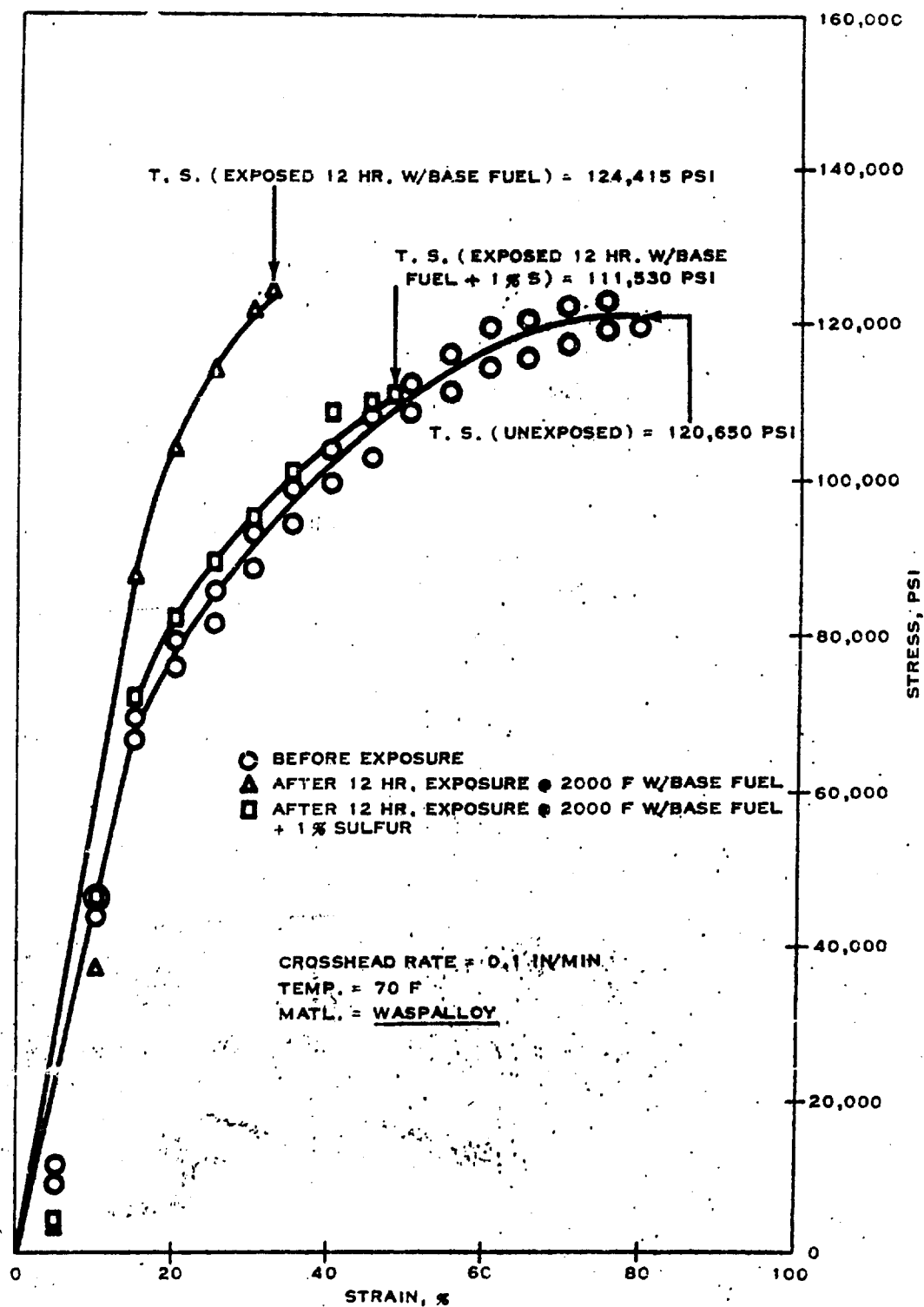


FIGURE 7
STRESS-STRAIN CURVE FOR WASPALLOY BEFORE AND AFTER 12 HOURS
EXPOSURE TO SULFUR-FREE AND SULFUROUS EXHAUST GAS @ 2000 F
IN THE PHILLIPS 2-INCH RESEARCH COMBUSTOR

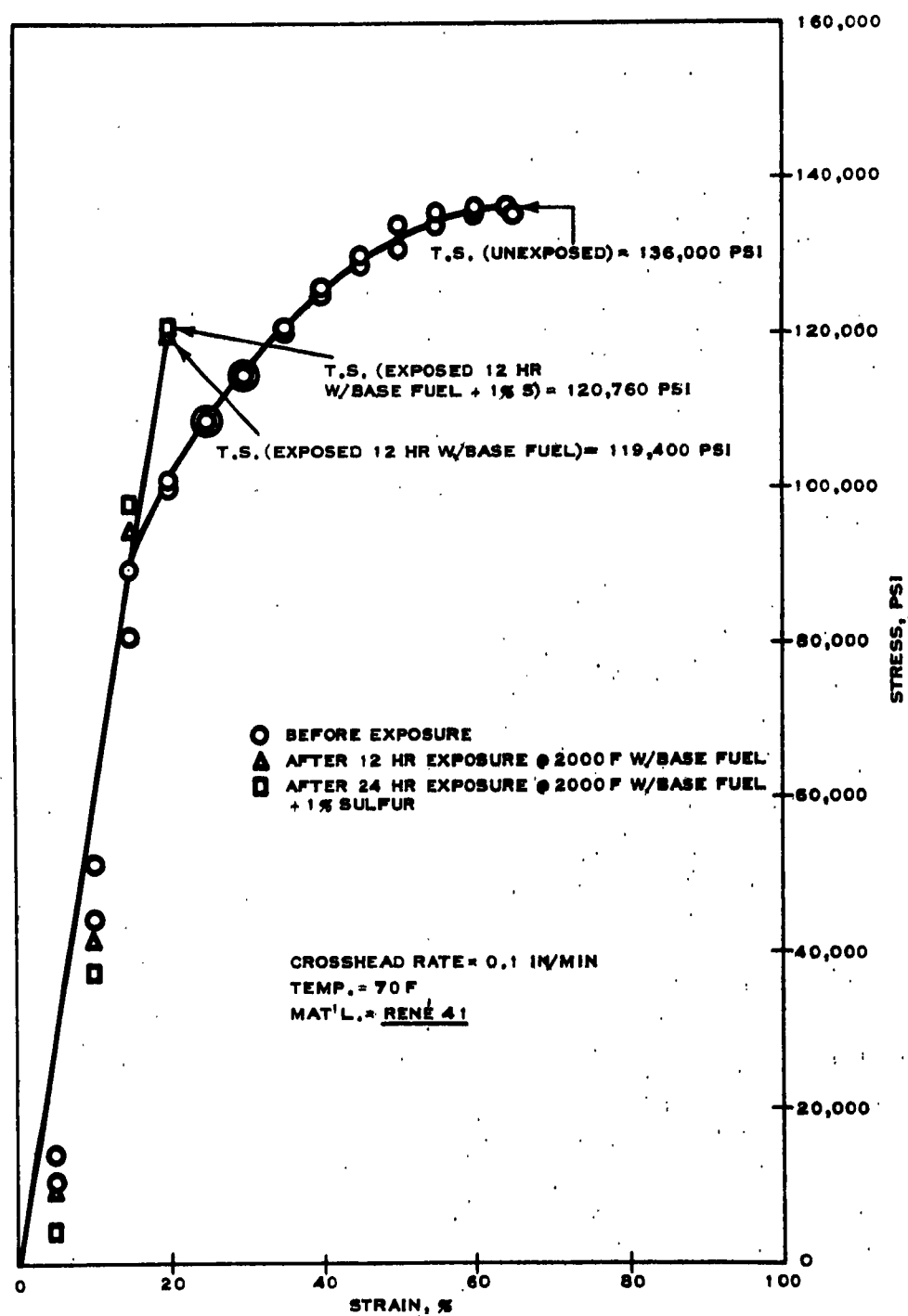


FIGURE 8
 STRESS-STRAIN CURVE FOR RENE 41 BEFORE AND AFTER 12 HOURS
 EXPOSURE TO SULFUR-FREE AND SULFUROUS EXHAUST GAS @ 2000 F IN
 THE PHILLIPS 2-INCH RESEARCH COMBUSTOR.

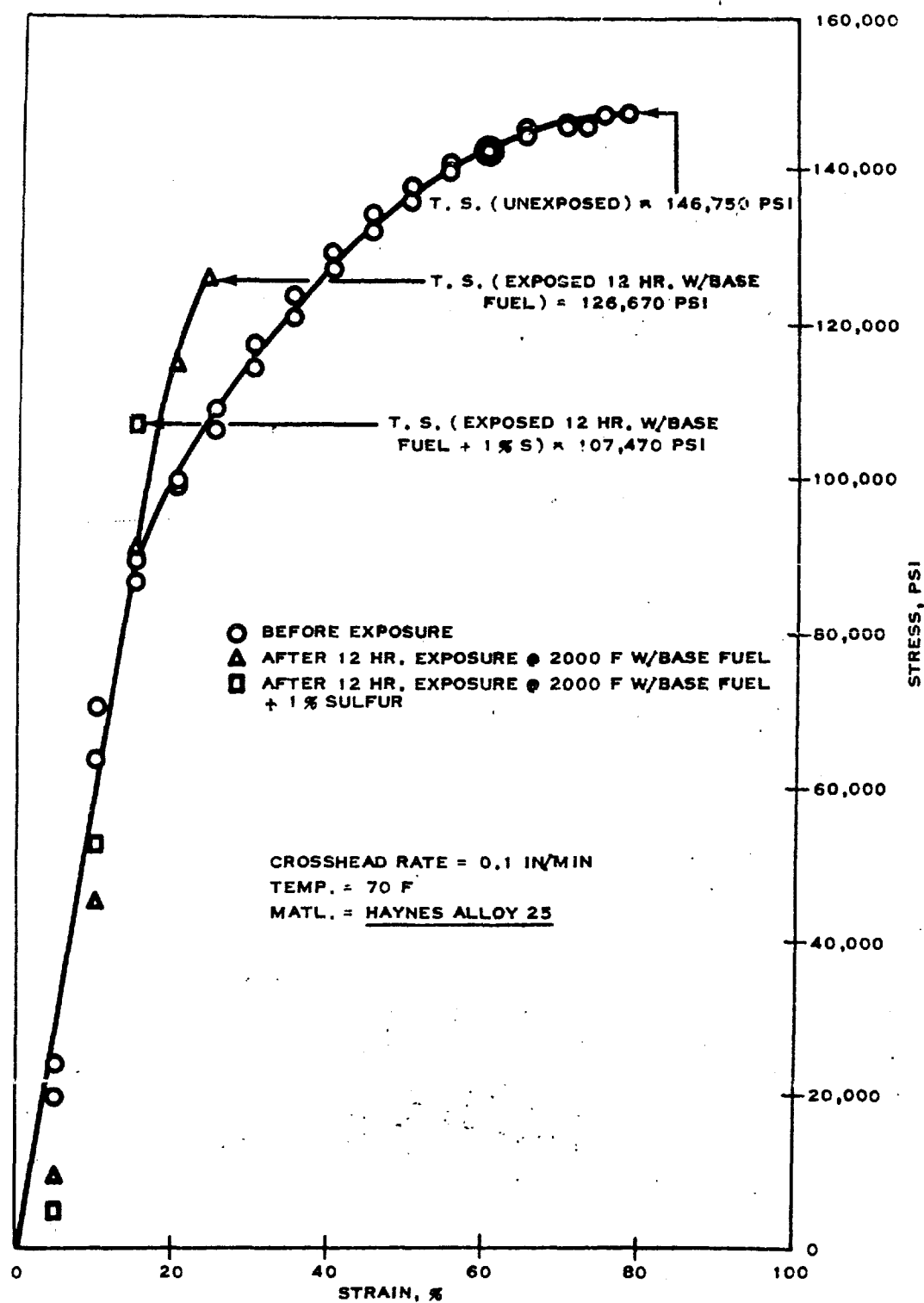


FIGURE 9
 STRESS-STRAIN CURVE FOR HAYNES ALLOY 25 BEFORE AND AFTER
 12 HOURS EXPOSURE TO SULFUR-FREE AND SULFUROUS EXHAUST GAS @ 2000 F
 IN THE PHILLIPS 2-INCH RESEARCH COMBUSTOR

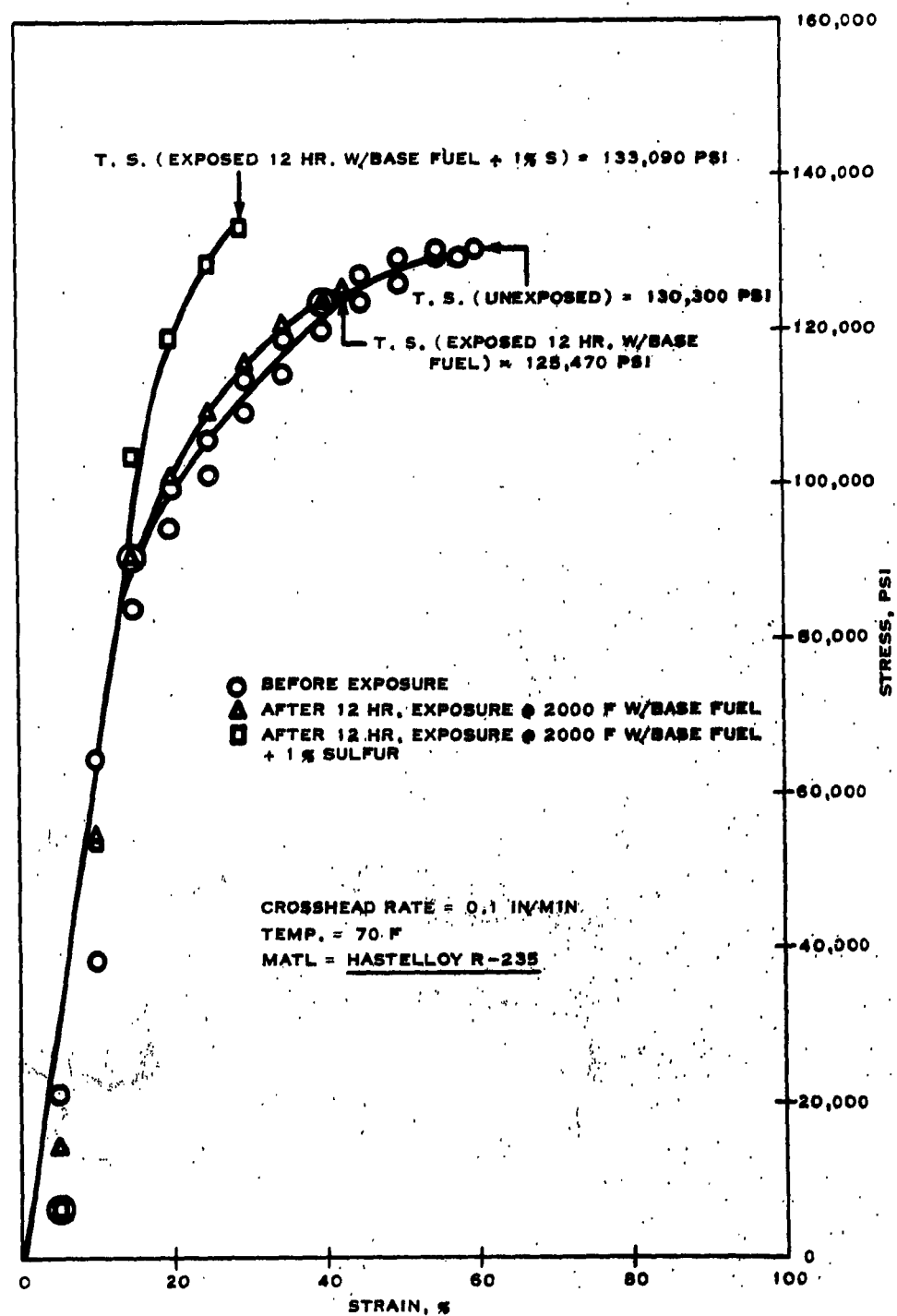


FIGURE 10
STRESS-STRAIN CURVE FOR HASTELLOY R-235 BEFORE AND AFTER 12 HOURS
EXPOSURE TO SULFUR-FREE AND SULFUROUS EXHAUST GAS @ 2000 F
IN THE PHILLIPS 2-INCH RESEARCH COMBUSTOR

greatest with Haynes Alloy 25, this material losing nearly twice as much strength with sulfur as without. The degradation of Waspalloy by sulfur is much less definite but is, at least, indicated. Calculations of the least significant difference (LSD) between a pair of observations (95 per cent confidence), when based upon the pooled standard deviation observed for the duplicate tests available on the unexposed samples, results in a value of 5750 psi. Thus, a pair of tensile strength values would have to differ by 5750 psi or more before one could justifiably conclude that a real difference exists. Consequently, the strength changes shown for Waspalloy and Hastelloy R-235 exposed to base fuel only and for Hastelloy R-235 exposed to base fuel plus 1.0 per cent sulfur are not believed significant.

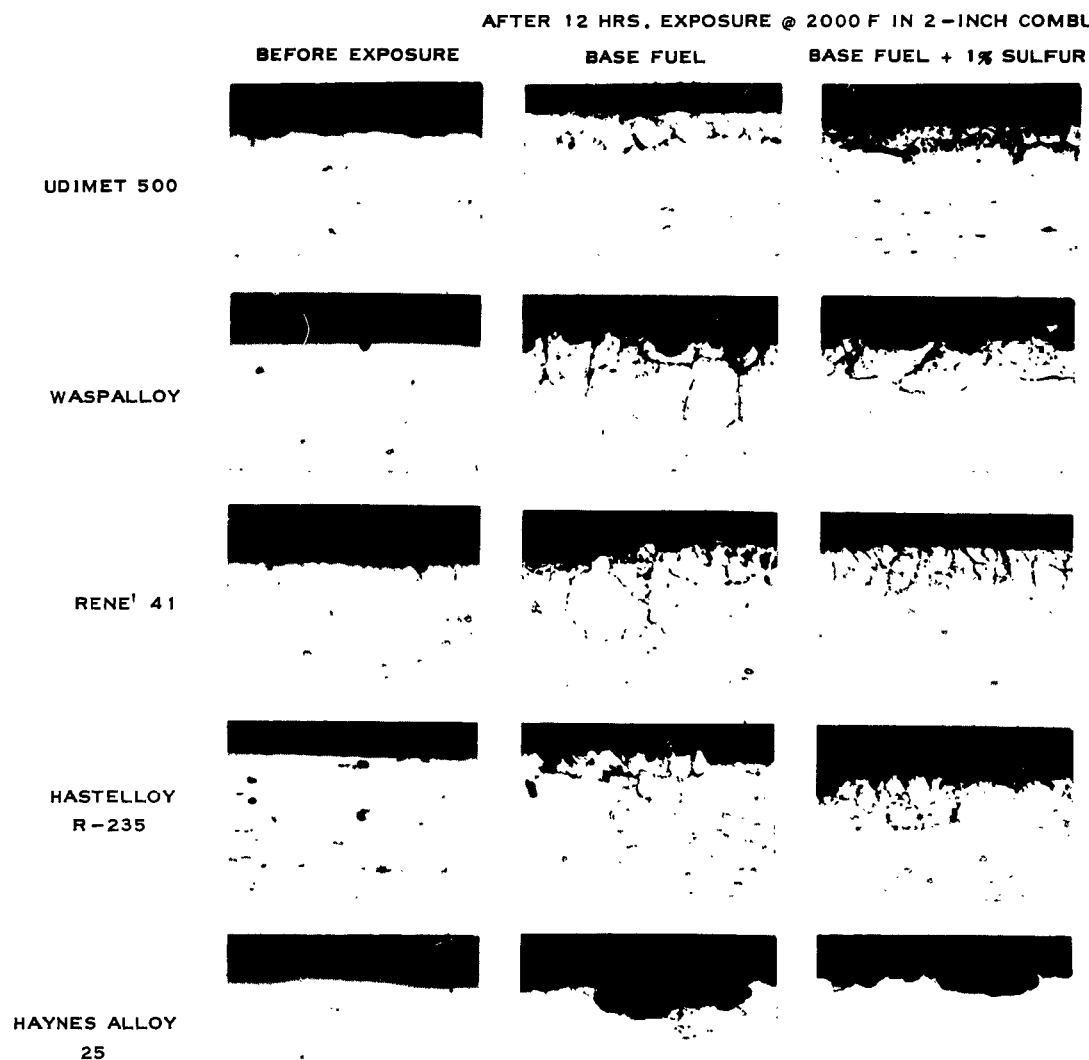
With the exception of the tensile data on Haynes Alloy 25, which differs from the balance of the alloys in that it is a cobalt-base alloy rather than nickel-base, these results do not provide a condemnation of fuel sulfur contamination from the standpoint of effects on component strength. Rather, they suggest a null effect of sulfur on tensile strength for the four nickel base alloys.

It will be observed from Figures 6, 7, 8, 9 and 10 that all of the alloys suffered marked losses in ductility after 12 hours exposure in the combustor with and without sulfur, as shown by the fact that all specimens failed at much lower strains than before exposure. In general, these losses were no greater with sulfur than without. Of additional interest is the fact that, in general, the "after exposure" curves followed the "before exposure" curves within the elastic range. One explanation of the decrease in ductility with loss in strength may lie in the possibility of intergranular oxidation during exposure in the combustor. These oxides might bestow little overall change in strength during elastic deformation, but be unable to withstand plastic deformation, thus resulting in failure

at both lower strains and lower stresses. As will be described below, most of the photomicrographs prepared from the exposed specimens do show evidence of intergranular attack, lending credence to this explanation.

Figures 11 and 12 show 200X magnification photomicrographs of the turbine guide vane corrosion specimens prepared before exposure and after exposure in the combustor to both sulfur-free and sulfurous exhaust gases at 2000 F. Figure 11 shows the unetched specimens and Figure 12 shows the same specimens after etching. In general, these pictures serve to support the data on metal loss and tensile strength-ductility loss previously discussed. Whenever any attack is evident in the pictures it appears to be primarily intergranular. In the case of exposure to the sulfur-free exhaust gases the attack is assumed to be intergranular oxidation. Although the photomicrographs of the sulfur-exposed specimens are remarkably similar to those prepared from specimens exposed to sulfur-free exhaust gases, it is not possible, lacking further analysis, to determine whether this attack is the result of intergranular sulfiding or intergranular oxidation. However, the similarity of the photomicrographs coupled with the metal loss data showing that sulfur did not accelerate metal losses at least suggests that oxidation may have been the mode of attack in both cases. Certainly the pictures in Figures 11 and 12 do serve to point out that, regardless of the mechanism of attack, damage was generally no greater with 1.0 per cent sulfur in the fuel than with the sulfur-free fuel.

With regard to the relative performance of the five alloys tested, the photomicrographs of Figures 11 and 12 suggest, as did the metal loss data previously discussed, that Haynes Alloy 25 was least attacked while Hastelloy R-235 was most attacked (this is particularly evident in the etched pictures with 1.0 per cent sulfur in the fuel).



MAGNIFICATION = 200X ; POLISHED - NO ETCHING

FIGURE 11
PHOTOMICROGRAPHS (BEFORE ETCHING) OF TURBINE GUIDE VANE SPECIMENS
BEFORE EXPOSURE AND AFTER 12 HOURS EXPOSURE IN THE PHILLIPS
2-INCH RESEARCH COMBUSTOR TO SULFUR-FREE AND SULFUROUS EXHAUST
GASES AT 2000 F

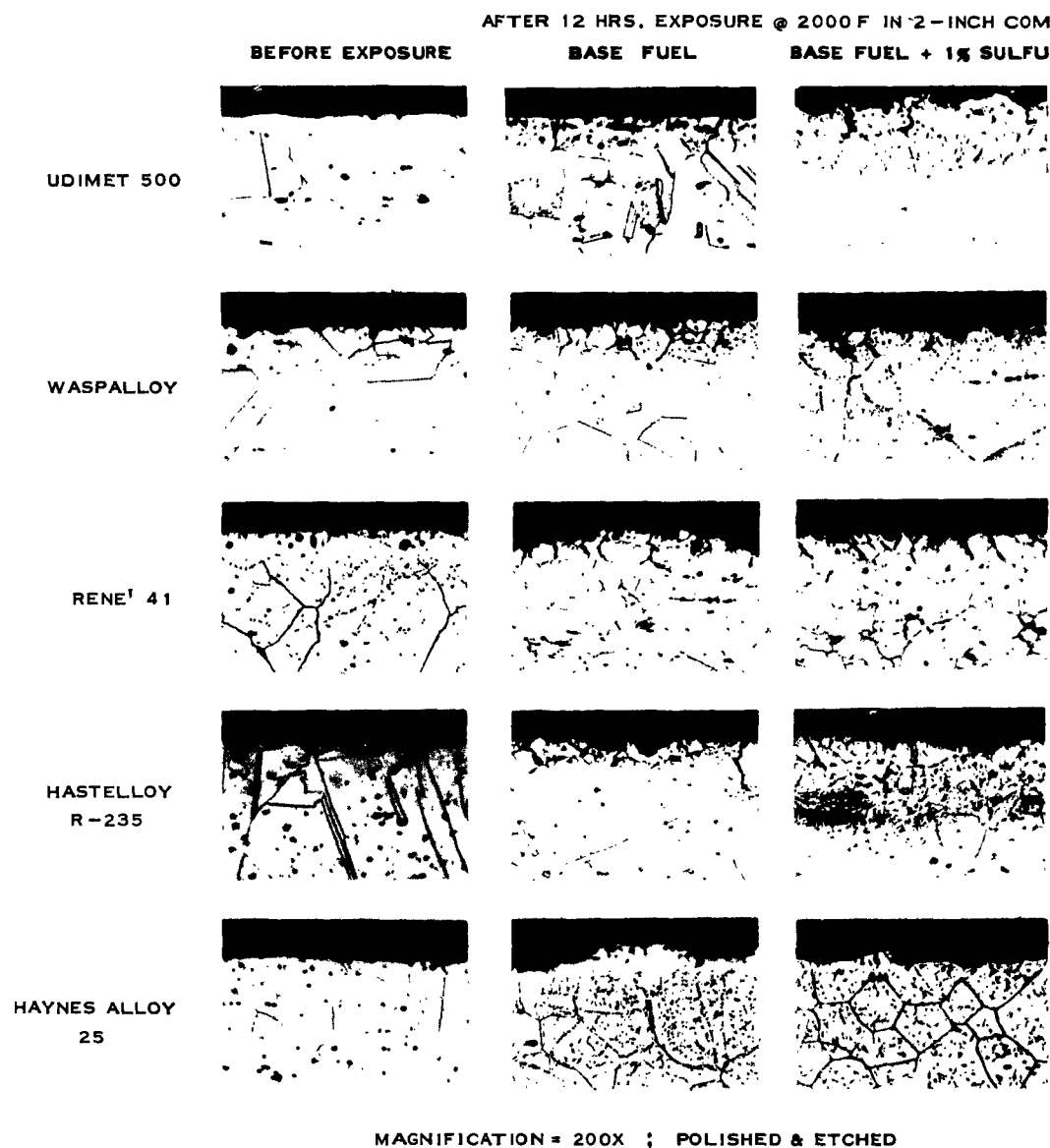


FIGURE 12
PHOTOMICROGRAPHS (AFTER ETCHING) OF TURBINE GUIDE VANE SPECIMENS
BEFORE EXPOSURE AND AFTER 12 HOURS EXPOSURE IN THE PHILLIPS
2-INCH RESEARCH COMBUSTOR TO SULFUR-FREE AND SULFUROUS EXHAUST
GASES AT 2000 F

B. Phillips Microburner Turbine Inlet Guide Vane Durability Tests

1. Test Procedure and Equipment

Some limited testing was carried on during this contract using the Phillips Microburner adapted for measuring metal losses from simulated turbine inlet guide vanes. It was intended that this Microburner data supplement the 2-inch combustor data and eventually provide a means for a more rapid evaluation of the effect of fuel and air contaminants on a variety of practical turbine blading alloys. The apparatus has been described in detail in (11). Briefly, this apparatus is 1.25-inch diameter atmospheric pressure tangential flow bench scale combustor. It is illustrated schematically in Figure 13. The exhaust system has been modified to allow placement of test materials in the exhaust stream. Simplified test pieces consisting of four $1/16$ " x $1/4$ " x $1-1/2$ " strips have been used. The position of these strips in the exhaust stream is illustrated in Figure 14. The holder containing the strips is clamped between the flanges shown in Figure 13. Exhaust gas temperature measurements are made by means of four equal area center thermocouples placed just up stream from the strips. The conditions of operation chosen for these tests were 500 F inlet air temperature, 25 fps inlet reference velocity and 0.055 fuel-air ratio which resulted in an exhaust gas temperature of 2000 ± 50 F at the plane of the test strips. This burner, incidentally, uses no secondary air. Determinations of weight losses from the test strips are made in the same way as in the 2-inch combustor tests. Weighings were made at 2 hour intervals for total test durations as high as 20 hours. The data are reported as combined weight loss per square centimeter of exposed area from all four test strips.

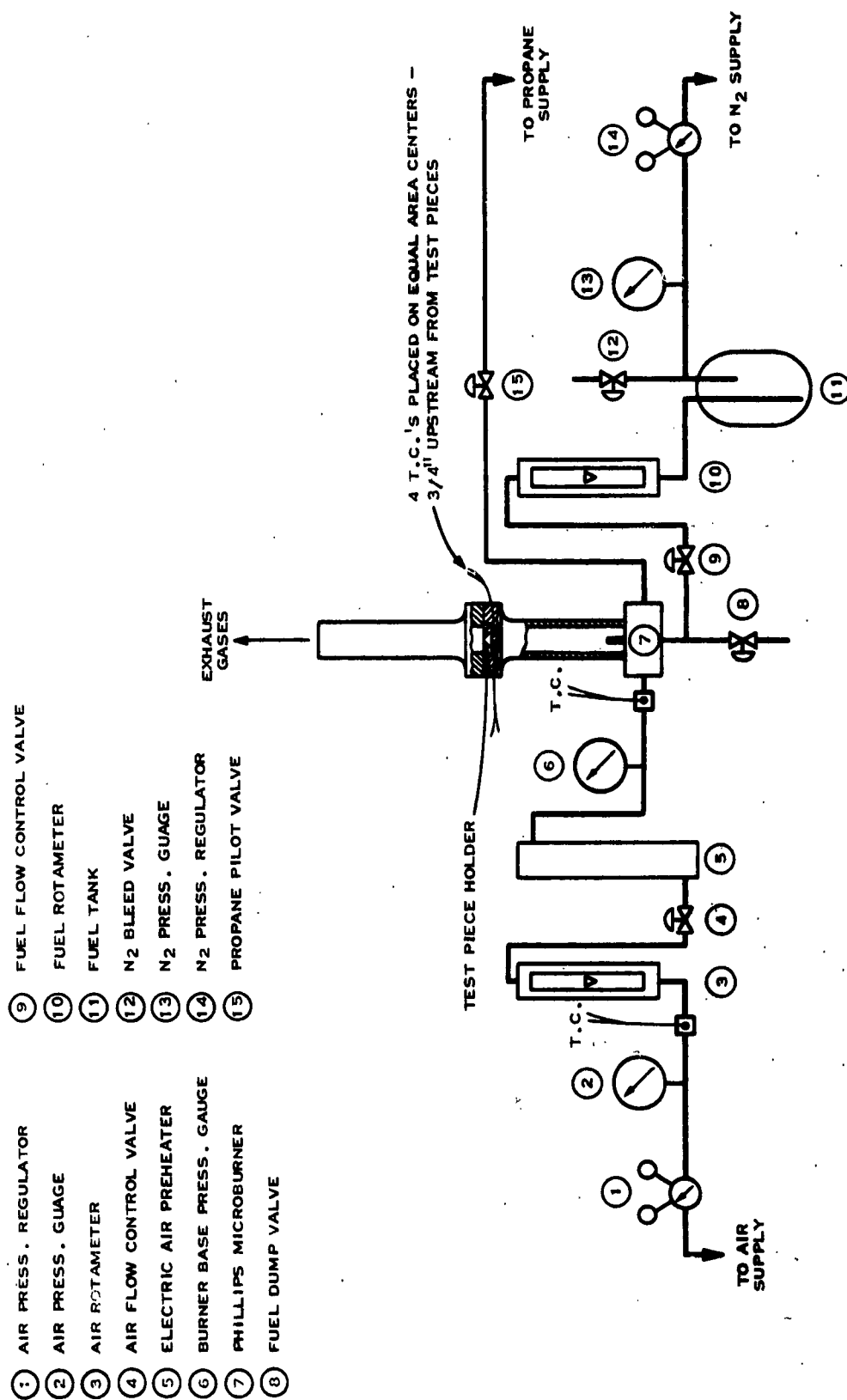
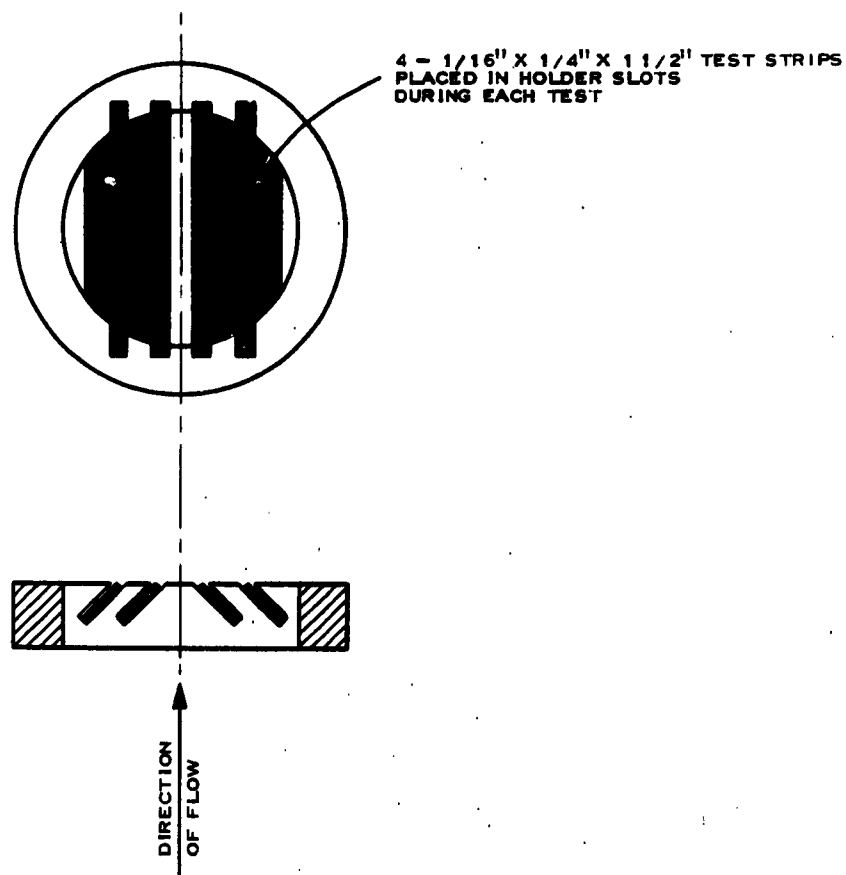


FIGURE 13
SCHEMATIC DIAGRAM OF PHILLIPS MICROBURNER ADAPTED FOR
MEASUREMENT OF TURBINE GUIDE VANE METAL DURABILITY

PHILLIPS PETROLEUM COMPANY
RESEARCH DIVISION REPORT 3529-63R



HOLDER MAT'L: 310 SS; STRIP MAT'L: VARIOUS TURBINE BLADING ALLOYS

SCALE: FULL

FIGURE 14
METAL DURABILITY SPECIMEN HOLDER FOR MICROBURNER APPARATUS

2. Results and Discussion

Results of the Microburner metal loss tests on Udimet 500, Waspalloy, Haynes Alloy 25 and Rene' 41 are shown in Figure 15 as plots of metal loss versus test duration. These data show some rather moderate tendency toward increased corrosion in the presence of 1.0 per cent fuel sulfur for test durations exceeding 14 hours. The most notable feature of the Microburner data, however, is the indication of pronounced detrimental effect of sulfur on Haynes Alloy 25. This was in evidence from the beginning of the test. It will be recalled that Haynes Alloy 25 showed no sulfur sensitivity in the 2-inch combustor test. It was, in fact, the best performing alloy (metal loss basis) of the group tested. It is believed, in light of the repeatedly low metal losses obtained with Haynes Alloy 25 in the 2-inch combustor, that the 1.0 per cent sulfur test on the Haynes Alloy 25 in the Microburner is subject to considerable doubt. It is possible that another material might have been accidentally substituted in this test. Otherwise these data correlate fairly well as shown in Figure 16.

The suggestion from these Microburner data that a test duration longer than six hours might be desirable for the metal loss tests in the 2-inch burner, in order to develop any indications of sulfur degradation, constituted justification for extending the 2-inch combustor metal loss tests from six hours to twelve hours. It will be recalled from the previous discussion of the 2-inch burner metal loss data, that no indication of degradation by fuel sulfur was found even after 12 hours test duration.

Although the Microburner demonstrated some applicability for evaluation of superalloy durability it was decided, upon completion of the foregoing tests, to discontinue Microburner testing due to budgetary and time considerations in order to allow more extensive testing in the

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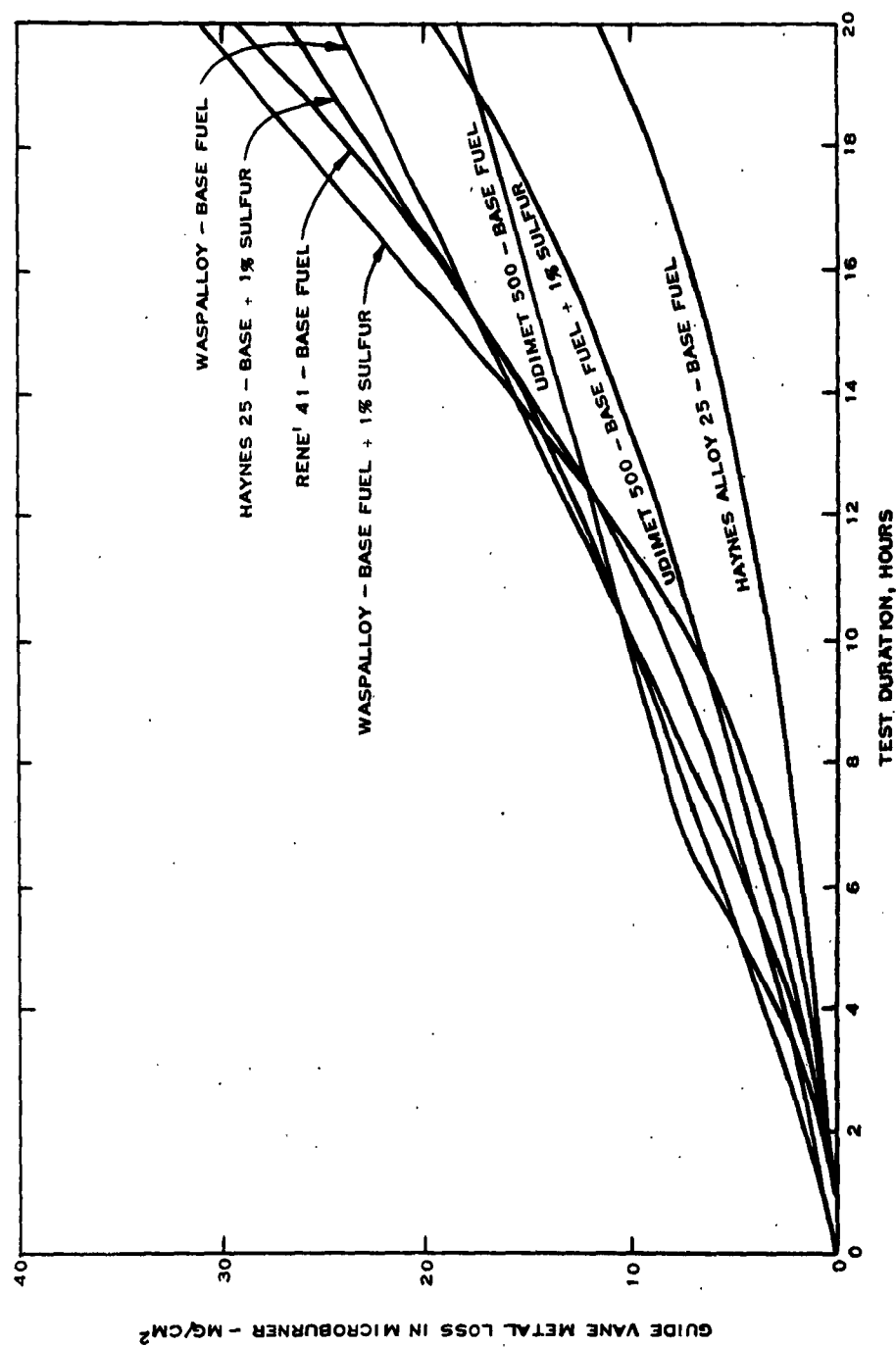
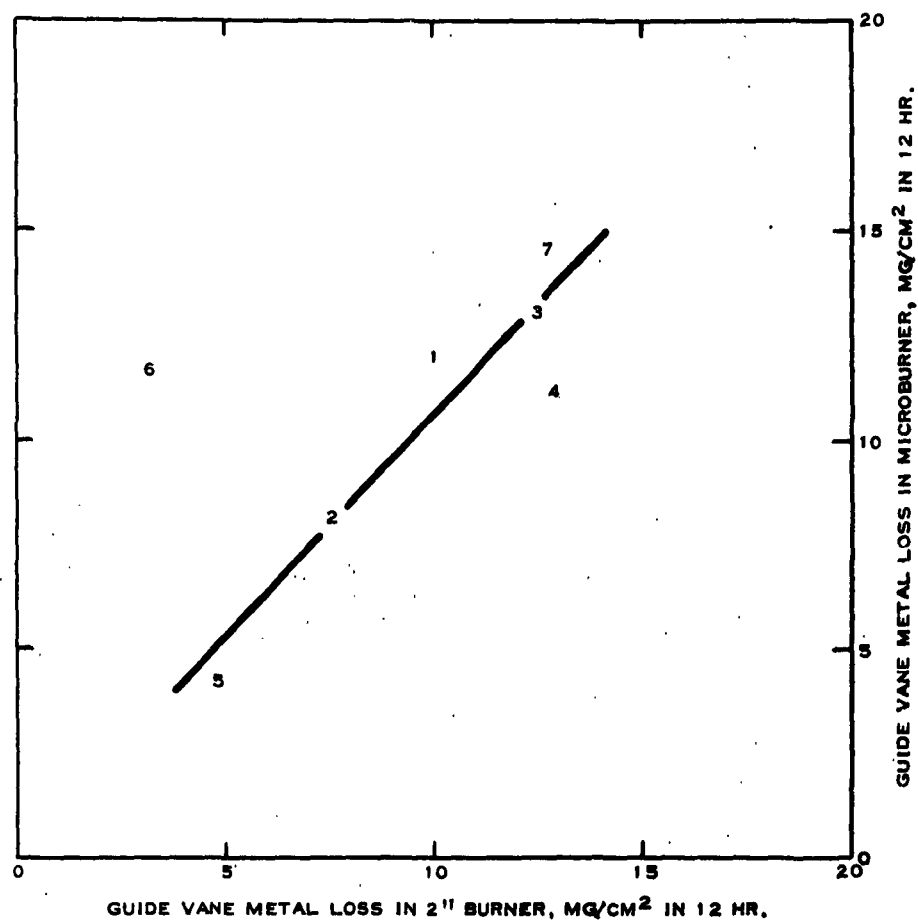


FIGURE 15
TURBINE GUIDE VANE METAL LOSS IN THE PHILLIPS MICROBURNER AS A
FUNCTION OF TEST DURATION

PHILLIPS PETROLEUM COMPANY
RESEARCH DIVISION REPORT 3529-63R



- 1 - UDIMET 500 - BASE FUEL
- 2 - UDIMET 500 - BASE FUEL + 1% SULFUR
- 3 - WASPALLOY - BASE FUEL
- 4 - WASPALLOY - BASE FUEL + 1% SULFUR
- 5 - HAYNES ALLOY 25 - BASE FUEL
- 6 - HAYNES ALLOY 25 - BASE FUEL + 1% SULFUR
- 7 - RENE' 41 - BASE FUEL

FIGURE 16
CORRELATION OF 2-INCH COMBUSTOR AND MICROBURNER GUIDE
VANE METAL LOSSES

Phillips 2-inch Combustor, which more nearly simulates actual operational conditions. At some time in the future, however, after a greater volume of metal durability data has been obtained in high pressure combustors, it may become desirable to resume testing with the Microburner in order to better establish whether or not a useful correlation exists between this atmospheric combustor and high pressure combustors.

C. Semi-Dynamic Furnace Tests on the Durability of Superalloys

1. Test Procedures and Equipment

An additional effort carried on during this contract involved an investigation, in bench scale apparatus, of sulfur corrosion of the type which has come to be known colloquially as "black plague". Since corrosive attack identified by other investigators (12, 13) as black plague had not been observed in this laboratory during repeated combustor testing in which sulfur was present both in the fuel and in ingested sea water (as Na_2SO_4), it was considered desirable to attempt to reproduce this type of corrosion under the conditions described by these investigators in order to better understand its nature, appearance, and the relative importance of the variables suggested as responsible for the attack. For this purpose a semi-dynamic furnace test was employed. A group of superalloys including Udimet 500, Rene' 41, Hastelloy R-235, Waspalloy, and Haynes Alloy 25 was evaluated at 2000 F in the presence of air, sulfur dioxide, carbon and sea salts individually and in all combinations.

Black plague sulfur attack has been pictured by some investigators (12) as a current problem in aviation gas turbines, although this has not been confirmed during discussions with personnel familiar with both Navy and Air Force aircraft field experience in the United States. Nevertheless, a number of laboratory investigations do suggest that this is a potential problem. It therefore appeared desirable to more closely define the causative factors, possible means of avoidance, and the relative performance of available alloys.

The bench scale method employed for this investigation was patterned after a method described by Bristol Siddeley Engines, Ltd. (12). In the Phillips version, metal specimens measuring $1/2$ " wide by $2\ 3/8$ " long by $1/16$ " thick are placed in porcelain boats $3/8$ " wide by 3" long by $1/4$ " deep. The boat containing the metal strip is placed in a two-inch tube furnace held at 2000 F. Air is flowed through the furnace for a period of 45 minutes followed by sulfur dioxide for 45 minutes. These gases are cycled 45 minutes each for a total duration of six hours. For tests involving the possible reducing effects of carbon, a $1/2$ " diameter by 2" long carbon rod is placed in the boat along side the metal strip and in contact with the surface of the strip. The tests which include sea salt are carried out by simply packing two grams of the salt around the metal specimen as it sits in the porcelain boat. The sea salt is prepared by blending dry salts together in the proportions specified in ASTM Method D665-60 for synthetic sea water. The salts used and their proportions are as follows:

<u>Component</u>	<u>% By Weight</u>
NaCl	58.49
MgCl ₂ ·6H ₂ O	26.46
Na ₂ SO ₄	9.75
CaCl ₂	2.76
KCl	1.64
NaHCO ₃	0.48
KBr	0.24
H ₃ BO ₃	0.07
SrCl ₂ ·6H ₂ O	0.10
NaF	0.01

In cases where sulfur dioxide is not used, air is continuously flowed through the furnace for the entire six-hour duration.

Evaluation of the extent of attack is based upon weight of metal loss (following rotary brush descaling) and on visual observation. These tests were run on each of the five superalloys with combinations of materials as follows: (1) air, (2) air + carbon, (3) air + sulfur dioxide, (4) air + sea salt, (5) air + carbon + sulfur dioxide, (6) air + sulfur dioxide + sea salt, (7) air + carbon + sea salt, (8) air + carbon + sulfur dioxide + sea salt.

This test method is admittedly severe as compared to actual conditions existing in engines. However, since the intent here is simply to demonstrate potentialities and to establish the relative importance of the several simulated fuel and/or air contaminants, it is believed to be a useful tool for the purpose.

2. Background Information on "Black Plague" Sulfur Attack as Obtained from the Literature

Black plague sulfur attack, as described in the literature (12, 13), is evidenced by dark-colored, raised blisters on the surface of the component. A green coloration may be present. In severe cases the raised attack may be nodular and possibly, in the case of a turbine blade, cover the whole of the concave side in the hottest region of the blade. Cracks may then appear in the area of the sulfur attack itself, for example, longitudinally on the leading edge or in a transverse direction at the trailing edge. These cracks may be restricted with little or no penetration into the sound core material.

A remarkable feature of this kind of attack is that turbine blades have, on occasion, suffered extremely severe attack without failure. This is attributed to the tendency of sulfur attack to advance on a broad front and hence it is by thinning of the section until the component is unable to withstand the applied stress that failure may ultimately occur, rather than by preferential attack of the stress corrosion type on the grain boundaries.

The microscopic appearance of sulfur attack has been described (12) by characteristic phases, although all phases are not always detectable. The following phases have been reported:

- (a) In front of the advancing corrosion products, light gray globules are evident. These are generally randomly distributed within the grains although they may also be in the grain boundaries if carbides have been precipitated, since these are rather susceptible to attack.
- (b) There follows a two phase region consisting of a light "metallic" phase intermingled with a darker gray material.
- (c) A mainly continuous zone, which is gray in appearance, is produced on the outer surface.
- (d) In laboratory experiments a phase which has apparently been liquid may also exude to the surface.

Although little concrete information is available, one reference (12) indicates that the metallic elements are present in the scale in the same relative proportions as in the parent material. Reports regarding the presence of sulfur on corroded blades produced by actual engine tests are rather variable, ranging from 0.5 per cent to slight or undetectable (12, 13). It has been demonstrated that the outermost layer of corrosion may have only a small sulfur content but that this may increase nearer the base metal.

The corrosion product has been reported to be very hard and brittle. It is adherent and occupies a considerably larger volume than the base material. Only after it becomes quite thick does it tend to crack and chip away under engine running conditions. It may sometimes be removed by vapor blasting or shot blasting, whereupon pitting may result.

X-ray diffraction analyses (12) have generally shown that the corrosion product consists predominantly of nickel oxide (NiO) together with a spinel of mainly nickel oxide and chromium oxide.

Sulfide has been detected on turbine blades using a technique of electron probe analysis. Evidence of sulfide has been found at the metal/oxide interface and a concentration of chromium at the grain boundaries. Titanium/molybdenum inclusions have been found away from the interface but not at the interface itself.

Particles chipped from corroded components are normally noticeably ferromagnetic and there is evidence that this is strongest in the intermediate zone where presumably the material is sufficiently nickel rich to produce this effect.

3. Postulated Mechanism of Attack

It would appear that there are approximately as many postulated mechanisms of sulfur attack as there are investigators in the field. However, the mechanism outlined below seems to enjoy fairly general acceptance and has been described by Betteridge (14) and also, in part, by Shirley (13).

The front of the attack consists of chromium sulfide (Cr_2S_3) the light gray globules detected on microscopic examination, dispersed in the parent material. Oxidation occurs to produce an intermediate layer of chromium oxide dispersed in nearly pure nickel, hence the ferromagnetism of the corrosion product. The outer layer appears to be a scale of nickel oxide, chromium oxide and the spinel, nickel chromite. With a continuous supply of sulfur, the nickel in the intermediate area may be attacked to produce a low melting point (1190 F) nickel/nickel sulfide eutectic which may exude out.

Many investigators in this field believe that a requisite for the initiation of the attack is that the film of chromium oxide on the surface, assumed to act as a protective barrier to subsurface attack, should be

broken down. This suggests that a reducing agent must be present. Unburned carbon could act to reduce the chromium oxide. If the sulfur is present in the form of a sulfate, which is relatively non-reactive, carbon could reduce this to the more reactive sulfide.

Shirley (13) has shown in his work that the attack is not related to direct sulfur absorption from gaseous combustion products but does occur through contact with chloride-contaminated alkali and alkaline earth sulfates, such as are present in sea salts. As little as 1 per cent chloride was found to induce a high rate of attack at 1300 to 1380 F. Considerably less attack was observed in the absence of chlorides.

4. Results and Discussion

Previous studies (4) of high temperature corrosion of superalloys conducted in the Phillips 2-Inch Research Combustor facility have shown little or no effect of as much as 1.0 per cent sulfur in the fuel and rather copious quantities of ingested sea water. Yet both verbal and written reports of a severe form of sulfur corrosion known colloquially as "black plague" continue to appear. As mentioned above, these reports generally assign large responsibility to the reducing effects of unburned carbon, from the standpoint of (1) possible destructive effect on protective chromium oxide surface films, and (2) reduction of the relatively non-reactive sulfates to the more reactive sulfides. It has also been suggested by some that sulfurous combustion gases might also be reduced by carbon to more reactive species. Therefore, the present tests were designed with two objectives in mind: (1) to reproduce the type of attack described by other investigators in order to afford a better understanding of its nature and the degree to which it may take place under very severe conditions, and (2) to assess the relative importance of the several factors postulated as responsible for the attack; namely, unburned carbon, ingested sea salt and/or fuel sulfur contamination.

Table IV shows the metal loss data obtained. Table V reports the visual appearance of scale formed and a visual estimate of the degree of attack. Table VI is a tabulation of the magnetic properties of each specimen before and after exposure at 2000 F to the indicated combinations of reactant variables.

The first objective of reproducing the type of attack described by others as "black plague" was accomplished in the present work. When appreciable attack of the alloys was observed it fit quite well the descriptions outlined in the literature, as may be seen from an inspection of Table V. There are, however, some apparent discrepancies in the metal loss data shown in Table IV when a comparison is made with the visual ratings of Table V. In several cases (a good example is Udimet 500 with air + carbon + SO₂) very severe attack was observed visually, while the metal losses were rather small. In these cases, reexamination of the descaled strips indicates that probably much of the damaged material was not removed by the wire brush descaling methods used in these tests, suggesting that, in future work, careful consideration should be given to other techniques such as cathodic descaling in molten caustic. In any case, these results point out the dangers of drawing conclusions on the basis of metal loss alone when attack as extensive as observed in many of these tests has occurred. Certainly, when metal losses were high the visual ratings indicated very severe attack, but the converse was not always true. It is believed that the results of this series of tests confirm the potentiality of extremely severe attack causing catastrophic failures.

Considering the results in terms of the relative importance of carbon, sulfur dioxide, and sea salt, it may be seen from Tables IV and V that, on an individual basis, only sea salt caused any significant attack

TABLE IV
EFFECT OF AIR, CARBON, SO₂, AND SEA SALTS ON TYPICAL SUPERALLOYS -
METAL LOSSES IN SIX HOURS IN 2000F FURNACE TESTS

Alloy	Metal Loss, mg/cm ²							
	Treatment							
	Air	Air + Carbon	Air + SO ₂	Air + Sea Salt	Air + Carbon + SO ₂	Air + Carbon + Sea Salt	Air + SO ₂ + Sea Salt	Air + Carbon + SO ₂ + Sea Salt
Waspalloy	2.8	2.3	4.8	30.2 (1)	16.5 (2)	23.8	120.8 (3)	140.1 (3)
Hastelloy R-235	2.0	4.0	4.0	29.3 (1)	2.9 (2)	39.4	47.5 (3)	76.9 (3)
Rene' 41	2.2	0.5	5.2	265.1 (3)	0.0 (2)	62.1 (2)	57.1 (3)	28.6 (1)
Haynes Alloy 25	1.8	2.0	5.6	67.5 (2)	37.8 (2)	21.1	21.5	82.3 (3)
Udimet 500	0.9	3.5	4.7	13.6	4.9 (3)	25.9 (1)	46.9 (3)	58.2 (3)

Notes: (1) Visual rating after descaling: Medium - Very Severe.
(2) Visual rating after descaling: Very Severe.
(3) Visual rating after descaling: Very Severe, Catastrophic.

TABLE V
EFFECT OF AIR, CARBON, SO₂ AND SEA SALTS AT 200°C. F ON TYPICAL SUPERALLOYS - VISUAL APPEARANCE OF SCALE AND VISUAL ESTIMATES OF DEGREE OF ATTACK

Alloy	Treatment	Visual Appearance of Scale			Surface Distortions*	Overall Visual Impression of Severity of Attack After Descaling**	
		Thickness	Loose or Adherent?	Color		Very Slight	Very Severe
Inconel 600	Air + Carbon	Very Thin	Adherent	Gray	Very Slight	Very Slight	Very Slight
	Air + SO ₂	Very Thin	Adherent	Gray	Very Slight	Very Slight	Very Slight
	Air + Sea Salt	Very Thin	Adherent	Gray	Very Slight	Very Slight	Very Slight
	Air + Carbon + SO ₂	Thick	Loose	Gray-Black w/Green Areas	Medium - Very Severe	Medium - Very Severe	Medium - Very Severe
	Air + SO ₂ + Sea Salt	Medium	Loose	Gray-Black w/Green Areas	Very Severe	Very Severe	Very Severe
	Air + Carbon + Sea Salt	Very Thick	Loose	Green & Black	Very Severe (Catastrophic)	Very Severe (Catastrophic)	Very Severe (Catastrophic)
	Air + Carbon + SO ₂ + Sea Salt	Very Thick	Loose	Black w/Green & Blue Areas	Yes (Very Severe)	Yes (Very Severe)	Yes (Very Severe)
	Air + Carbon	Very Thin	Adherent	Gray	Very Slight	Very Slight	Very Slight
	Air + SO ₂	Very Thin	Adherent	Gray	Very Slight	Very Slight	Very Slight
	Air + Sea Salt	Medium	Loose	Green	Medium - Severe	Medium - Severe	Medium - Severe
Inconel 700	Air + Carbon + SO ₂	Thick	Loose	Gray - Black	Very Severe - Slight	Very Severe - Slight	Very Severe - Slight
	Air + SO ₂ + Sea Salt	Thick	Loose	Black w/Blue & Peacock	Very Severe (Catastrophic)	Very Severe (Catastrophic)	Very Severe (Catastrophic)
	Air + Carbon + Sea Salt	Very Thick	Loose	Black w/Peacock	Very Severe (Catastrophic)	Very Severe (Catastrophic)	Very Severe (Catastrophic)
	Air + Carbon + SO ₂ + Sea Salt	Very Thick	Loose	Black w/Green Areas	Yes (Very Severe)	Yes (Very Severe)	Yes (Very Severe)
	Air + Carbon	Very Thin	Adherent	Gray	Very Slight	Very Slight	Very Slight
	Air + SO ₂	Very Thin	Adherent	Gray	Very Slight	Very Slight	Very Slight
	Air + Sea Salt	Medium	Loose	Green	Medium - Severe	Medium - Severe	Medium - Severe
	Air + Carbon + SO ₂	Thick	Loose	Gray - Black	Very Severe - Slight	Very Severe - Slight	Very Severe - Slight
	Air + SO ₂ + Sea Salt	Thick	Loose	Black w/Blue & Peacock	Very Severe (Catastrophic)	Very Severe (Catastrophic)	Very Severe (Catastrophic)
	Air + Carbon + Sea Salt	Very Thick	Loose	Black w/Peacock	Very Severe (Catastrophic)	Very Severe (Catastrophic)	Very Severe (Catastrophic)
Inconel 718	Air + Carbon	Very Thin	Adherent	Gray	Very Slight	Very Slight	Very Slight
	Air + SO ₂	Very Thin	Adherent	Gray	Very Slight	Very Slight	Very Slight
	Air + Sea Salt	Medium	Loose	Green	Medium - Severe	Medium - Severe	Medium - Severe
	Air + Carbon + SO ₂	Thick	Loose	Gray - Black	Very Severe - Slight	Very Severe - Slight	Very Severe - Slight
	Air + SO ₂ + Sea Salt	Thick	Loose	Black w/Blue & Peacock	Very Severe (Catastrophic)	Very Severe (Catastrophic)	Very Severe (Catastrophic)
	Air + Carbon + Sea Salt	Very Thick	Loose	Black w/Peacock	Very Severe (Catastrophic)	Very Severe (Catastrophic)	Very Severe (Catastrophic)
	Air + Carbon + SO ₂ + Sea Salt	Very Thick	Loose	Black w/Green Areas	Yes (Very Severe)	Yes (Very Severe)	Yes (Very Severe)
	Air + Carbon	Very Thin	Adherent	Gray	Very Slight	Very Slight	Very Slight
	Air + SO ₂	Very Thin	Adherent	Gray	Very Slight	Very Slight	Very Slight
	Air + Sea Salt	Medium	Loose	Green	Medium - Severe	Medium - Severe	Medium - Severe
Haynes Alloy 25	Air + Carbon	Very Thin	Adherent	Gray	Very Slight	Very Slight	Very Slight
	Air + SO ₂	Very Thin	Adherent	Gray	Very Slight	Very Slight	Very Slight
	Air + Sea Salt	Medium	Loose	Green	Medium - Severe	Medium - Severe	Medium - Severe
	Air + Carbon + SO ₂	Thick	Loose	Gray-Black w/Green Areas	Very Severe (Almost Destroyed)	Very Severe (Almost Destroyed)	Very Severe (Almost Destroyed)
	Air + SO ₂ + Sea Salt	Thick	Loose	Black w/Peacock	Very Severe	Very Severe	Very Severe
	Air + Carbon + Sea Salt	Very Thick	Loose	Black w/Peacock	Very Severe (Catastrophic)	Very Severe (Catastrophic)	Very Severe (Catastrophic)
	Air + Carbon + SO ₂ + Sea Salt	Very Thick	Loose	Black w/Peacock & Blue	Yes (Very Severe)	Yes (Very Severe)	Yes (Very Severe)
	Air + Carbon	Very Thin	Adherent	Black	Very Slight	Very Slight	Very Slight
	Air + SO ₂	Very Thin	Adherent	Black	Very Slight	Very Slight	Very Slight
	Air + Sea Salt	Medium	Loose	Blue w/Blue Areas	Very Severe	Very Severe	Very Severe
Unalut 5/C	Air + Carbon	Very Thin	Adherent	Black	Very Slight	Very Slight	Very Slight
	Air + SO ₂	Very Thin	Adherent	Black	Very Slight	Very Slight	Very Slight
	Air + Sea Salt	Medium	Loose	Blue w/Blue Areas	Very Severe	Very Severe	Very Severe
	Air + Carbon + SO ₂	Thick	Loose	Black w/Blue Areas	Very Severe	Very Severe	Very Severe
	Air + SO ₂ + Sea Salt	Thick	Loose	Black w/Blue Areas	Very Severe	Very Severe	Very Severe
	Air + Carbon + Sea Salt	Very Thick	Loose	Black w/Blue Areas	Very Severe	Very Severe	Very Severe
	Air + Carbon + SO ₂ + Sea Salt	Very Thick	Loose	Black w/Blue Areas	Very Severe	Very Severe	Very Severe
	Air + Carbon	Very Thin	Adherent	Gray	Very Slight	Very Slight	Very Slight
	Air + SO ₂	Very Thin	Adherent	Gray	Very Slight	Very Slight	Very Slight
	Air + Sea Salt	Medium	Loose	Gray-Black w/Green Areas	Very Slight	Very Slight	Very Slight

* Ratings may be very thin, thin, medium, thick, very thick.
** Ratings may be very slight, slight, medium, severe, very severe.

relative to the "air only" base line. Sulfur dioxide did show some tendency to cause increased corrosion, although this was very slight compared to the sharp increases in attack experienced during the air + sea salt runs. In this case, as in others to be discussed, the effect of sea salt was quite specific to certain alloys. Rene' 41, for example, was almost completely destroyed during the air + sea salt run, while Udimet 500 showed only slight to medium attack.

The detrimental effect of the presence of carbon as a postulated reducing agent for protective chromium oxide films was confirmed in the test with air + carbon + sulfur dioxide. Although neither carbon nor sulfur dioxide, by themselves, appeared significantly detrimental, together they brought about severe to very severe attack of all of the alloys. An interesting aspect of these tests is the fact that the metal losses did not reflect the severity of corrosion. The surface scale produced during these runs appeared to be loose, flaky, and thick, but attempts to remove this scale showed that much of the sub-surface scale was actually adherent. Although extensive damage had been done, particularly to Udimet 500, as shown by the badly distorted surfaces, the metal losses did not reveal this because of the adherence of some of the corrosion products. It was also obvious that the greatest damage occurred over areas that were in direct contact with carbon.

Carbon also showed a tendency to accelerate sea salt corrosion as shown by the air + carbon + sea salt data in Tables IV and V on Waspalloy, Hastelloy R-235 and Udimet 500. However, there were two exceptions, Rene' 41 and Haynes Alloy 25, which indicated very pronounced inhibition attributable to the carbon. This was most apparent on a metal loss basis. Even so, the condition of the Rene' 41 test strip was still considered as representative of catastrophic failure following the test with carbon and sea salt.

When sulfur was provided by both sulfur dioxide and sea salts (no carbon) results varied from mild acceleration by the added SO₂ in the case of the Udimet 500 to apparent inhibition of the sea salt corrosion with Rene' 41 (although the R 41 was still badly corroded). At this point it should be noted that inhibition of the sea salt attack on Rene' 41 was indicated for both sulfur dioxide and carbon. This was also true to a lesser extent in the case of Haynes Alloy 25. The reason for this effect is not obvious from the composition of these alloys, but it was, nevertheless, again borne out when carbon was added while supplying both sea salts and sulfur dioxide. In these tests attack was definitely accelerated by the carbon, except in the case of Rene' 41 where, again, the attack was apparently inhibited by both carbon and sulfur dioxide. Except for Rene' 41 this combination of corrodents, air + carbon + sulfur dioxide + sea salts, was the most severe condition investigated, the balance of the alloys suffering catastrophic corrosion (approaching complete disintegration).

Of the forty tests involved in this program by far the most spectacular results occurred in the test where Rene' 41 was exposed to air + sea salt. It seems desirable at this point to emphasize the fact that approximately 40 per cent of the original weight of the test specimens was lost in this test, showing the potential effect this single corrodent could have on certain alloys in jet engine "hot section" components without the presence of unburned carbon or fuel sulfur.

With respect to the relative performance of the five alloys tested, these data show that no single alloy performed well in all situations. Overall, however, Udimet 500 performed best of the group.

Before and after exposure in the furnace each strip was checked for ferromagnetic properties after descaling. The results are shown in Table VI. None of the metals exhibited appreciable magnetic properties

TABLE VI
MAGNETIC PROPERTIES OF SUPERALLOYS BEFORE AND AFTER FURNACE TESTING AT 2000F

Alloy	Before Exposure	Air	Air + Carbon	Air + SO ₂	Air + Sea Salt	Air + Carbon + SO ₂	Air + SO ₂ + Sea Salt	Air + Carbon + Sea Salt	Air + Carbon + SO ₂ + Sea Salt
Waspalloy	NM	NM	NM	NM	NM	M	NM	NM	M
Hastelloy R-235	NM	NM	NM	NM	NM	M	M	NM	M
Rene' 41	NM	NM	NM	NM	NM	NM	NM	NM	NM
Haynes Alloy 25	NM	NM	NM	NM	NM	M	NM	NM	M
Udimet 500	NM	NM	NM	NM	NM	M	M	NM	M

Code: NM = non-magnetic or so slightly magnetic as to be negligible.

M = magnetic

before exposure, or after exposure to air, air + carbon, air + sulfur dioxide or air + sea salt. All except Rene' 41 (which remained consistently non-magnetic) were strongly magnetic following exposure to air + carbon + sulfur dioxide and the property was most pronounced in the areas of the strips that were the most severely corroded. Exactly the same results were observed in the test with air + carbon + sulfur dioxide + sea salts, but with air + sulfur dioxide + sea salt only two alloys, Hastelloy R-235 and Udimet 500, became magnetic. With air + carbon + sea salt all of the materials remained non-magnetic. Although there seem to be some inconsistencies in these data, sulfur dioxide is the common factor in those tests in which magnetic properties developed in the alloys. Checks for magnetic properties in samples of the scales removed from each strip showed that all were non-magnetic.

The interesting thing about these data is that, contrary to the findings of other investigators, the remaining metal, rather than the scale, became magnetic, suggesting that the metal had become enriched in magnetic metals such as nickel and/or cobalt by virtue of losses in the non-magnetic alloying elements as the result of corrosion. In other words, it would appear that nickel and/or cobalt were not attacked as much as some of the other alloying elements. This, of course, does not fit the previously outlined mechanism of attack postulated by many. It does, however, fit the results of earlier work conducted by Phillips (15) which has shown the importance of high nickel content in alloys exposed to high temperature sulfurous atmospheres.

III. SPECIFICATION OF JET FUEL HYDROGEN CONTENT FOR CONTROL OF COMBUSTION CLEANLINESS

An additional task undertaken during this contract has been that of a critical analysis of the present test methods, Smoke Point (16) and Luminometer Number (17), which are used to evaluate the burning quality of hydrocarbon fuels for jet aircraft gas turbine engines. Both are performance tests in which a sample of jet fuel is burned in a wick lamp to determine its relative soot forming tendencies. Unfortunately, the laminar flow diffusion flame of the wick lamp differs significantly from the highly turbulent combustion process in an aircraft gas turbine engine. Comparisons of relative fuel performance have been used herein to illustrate differences in cleanliness between the various types of combustion processes.

The ratings of fuels by present test methods have been correlated with measurements of their cleanliness in full-scale aircraft gas turbine combustors. Similar correlations of performance with the hydrogen content of these fuels will also be shown. Comparisons of these correlations indicate that hydrogen content provides a superior measure of combustion cleanliness for jet fuels. This can be rationalized, using an admittedly oversimplified mechanism for soot formation in flames. If the significant reactions are visualized as competitive oxidation and dehydrogenation processes, the hydrocarbon molecule can either (a) fragment to oxides of carbon, (b) polymerize to large polybenzenoid structures (soot). The greater the hydrogen content of the fuel molecule, the greater the alteration in structure that is required before condensation can take place, and the more likely that oxidation will permit soot formation. The cleanest burning fuel should be the one which contains the most hydrogen.

A specification based upon a fundamental fuel property, such as hydrogen content, rather than a performance test, such as sooting tendency,

offers additional advantages. Hydrogen content can be determined accurately by a variety of test methods, allowing a selection from differing procedures and equipment to best meet the needs of research, process control, and product inspection. The basic guidance it provides, with respect to the requirement of refinery processes for upgrading jet fuel burning quality, may be easily understood by the petroleum chemist. Therefore, the use of hydrogen content for specification of the combustion cleanliness of jet fuels is encouraged.

A. Effect of Hydrocarbon Structure on Combustion Cleanliness

Combustion processes in diffusion flames and premixed flames are quite different. These differences are known to affect the relative tendencies of various hydrocarbon fuels to form soot. This is important because the burning qualities of jet fuels are currently specified by performance test methods using diffusion flames.

Diffusion flames are characterized by separation of fuel and oxygen by a wedge of combustion products. The chemical reaction at the interface does not control the rate of the combustion process. Diffusion processes require a relatively long time for completion. The fuel is decomposed thermally while diffusing to the reaction interface. The resultant high concentration of hydrocarbon radicals favors formation of soot.

Premixed flames are essentially explosion waves traveling through intimate mixtures of fuel and oxygen. Oxygen attacks the hydrocarbon molecule to produce highly reactive fragments which normally are broken down to oxides of carbon by sustained attack. However, the combustion process may be limited by a very short residence time in the flame zone or by an insufficient amount of oxygen in the mixture.

The distinguishing features of diffusion flames and premixed flames are less apparent under turbulent flow conditions. The vortices and the regular movements cause entrainment and mixing of fuel and oxygen in

turbulent diffusion flames. Such is the condition in an aircraft gas turbine combustor where the highly turbulent flame zone is fed by jets of air and fuel and is maintained by recirculating hot combustion products.

1. Diffusion Flames

A simple wick lamp has a diffusion flame in which fuel and air are not premixed. Small flames may be non-luminous. In larger flames the blue reaction zone gives way to a luminous tip. In still larger flames the soot particles formed in the luminous zone can grow so large that they are not oxidized at the reaction interface and escape in the flame as smoke. The height of the flame just before it begins to smoke is the index of burning quality in the present ASTM Method of Test for Smoke Point of Aviation Turbine Fuels (16).

The ASTM Smoke Point Method evolved from work done by Kewley and Jackson (18) some thirty years ago, in which they measured the relative burning quality of illuminating oils. They observed that the candle power of the flame in a wick lamp was directly proportional to flame height. Since flame height is much easier to measure than flame radiation, the maximum height to which the flame could be adjusted without smoking was chosen as an index of burning quality. Minchin (19) used this same apparatus a few years later to demonstrate that the relative "tendency to smoke" is a function of molecular structure. He constructed a chart for homologous series of hydrocarbons showing paraffins, naphthenes, olefins, monocyclic aromatics, and polycyclic aromatics in order of increasing tendency to smoke. The Institute of Petroleum Technologists shortly standardized the test method for measuring the smoke point of kerosine (20).

The wick lamp from the Weber potentiometer was used by Kewley and Jackson, probably because its small round wick is easily trimmed. IPT modified their apparatus slightly and ASTM adopted it without change. Following a study of the variables in the design of the wick lamp that affect

smoke point, Rakowsky and Hunt (21) developed the Indiana Smoke Point Lamp to have maximum sensitivity in the range of jet fuel quality requirements. They found an excellent correlation between fuel ratings with this lamp and the IPT lamp. The Indiana Lamp was subsequently used by Hunt (22) to investigate the relation of smoke point to molecular structure. Its increased sensitivity was used to advantage in studying homologous series of paraffin hydrocarbons. Normal paraffins were the cleanest burning hydrocarbons in a wick lamp, and the tendency to smoke was increased by methyl branching.

Clarke, Hunter and Garner (23) used a cone burner to investigate the effect of molecular structure on the tendency to smoke. This is a wickless lamp, with the flame burning freely in air from the surface of a pool of liquid fuel contained in a shallow funnel-shaped vessel. The height of the diffusion flame can be adjusted by varying the liquid level in the cone to change the surface area of fuel. They observe that the tendency to smoke increased with the compactness of the hydrocarbon molecule, in agreement with performance in wick lamps.

Schalla and McDonald (24) determined the effect of fuel prevaporization during their study of the effect of molecular structure on the tendency to smoke. They found that the maximum rate at which a hydrocarbon burned without producing smoke was independent of whether it was prevaporized and burned as a diffusion flame from a tube in still air or burned as a liquid in a wick lamp. They concluded that the smoking tendency of hydrocarbon is related directly to the stability of its carbon skeleton, and thereby to the ease of hydrogen atom removal. This agrees with previous experimental findings on the effect of molecular structure for diffusion flames.

Minchin (25) studied the effect of varying the aromatic content of fuels burned in a wick lamp on the luminosity of flames at their smoke

point. It was well known that the quantity of light available from the relatively large flames obtainable with paraffinic fuels was much greater than with aromatic fuels. However, Minchin showed that the candle power per unit area of flame for an aromatic fuel (tetralin) was nearly double that from a pure paraffin. His oversimplified conclusion was that the concentration of soot particles per unit volume of luminous flame tip doubled with tetralin.

The recent Method of Test for Luminometer Numbers of Aviation Turbine Fuels (17) rates fuels at a constant level of flame luminosity, and presumably at a constant soot content in the luminous flame tip. The size of the flame is measured indirectly by determining the temperature rise across a modified Smoke Point lamp. Bachman (26) studied the relation of Luminometer Number to molecular structure and concluded that burning quality as measured by the Luminometer was identical with that established previously on the basis of Smoke Point. Its claim to measuring the flame radiation characteristics of aviation turbine fuels has been questioned by Schirmer (27), since the Luminometer does not measure total flame radiant energy, nor any valid index thereof. Smoke Point and Luminometer Number test methods differ only in their technique for determining the soot point, and not in the basic phenomena being measured.

Studies of the effect of molecular structure on the sooting tendency of hydrocarbons in diffusion flames show consistently that normal paraffins burn significantly cleaner than their branched chain isomers. Generally, the difference between normal heptane and isooctane covers about half the performance range of the apparatus, if for reference purposes its lower limit is established by toluene or tetralin. Data from the work of Hunt (22), Clarke (23), and Bachman (26) are presented in Table VII to illustrate this difference between paraffins.

TABLE VII
COMBUSTION CLEANLINESS OF DIFFUSION FLAMES

<u>Hydrocarbon</u>	<u>Indiana Smoke Point, mm</u>	<u>Cone Burner Smoke Point, cm</u>	<u>Luminometer Number</u>
Normal Heptane	147	15.9	224
Isooctane	86	6.3	100
Toluene	6	1.0	3
Tetralin	6	1.2	0

2. Premixed Flames

Conditions are much less favorable for the formation of soot in premixed flames, because fuel and oxygen are intimately mixed prior to reaction. Soot formation reactions must compete with the more rapid oxidation reactions for the carbon atoms. However, the deficiency of oxygen in premixed flames of rich fuel-air mixtures can leave hydrocarbon fragments to form soot.

An ordinary laboratory Bunsen burner does not exhibit a true premixed flame, diffusion of surrounding air into the flame is substantial and alters the mixture strength at which soot can be formed, if at all. The classical solution has been to place an outer jacket around the flame, sealing it to the barrel of the Bunsen burner to prevent air entrainment. This allows the premixed gases to burn in an atmosphere of their own combustion products. Smithells and Ingle first used this arrangement around 1892 to study the true structure of premixed hydrocarbon-air flames (28). It is commonly referred to as Smithells' flame separator because a secondary diffusion flame can be supported from the top of the outer jacket if the primary fuel-air mixture is rich enough.

Street and Thomas (29) used a Smithells' separator to study the effect of molecular structure on the sooting tendency of premixed hydrocarbon-air flames. The critical concentration of air required to suppress flame

luminosity was the index of sooting tendency. A ratio of this amount of oxygen to that required for stoichiometric combustion to carbon dioxide and water was used for comparing relative combustion cleanliness. As with diffusion flames, hydrocarbon structure was found to be important, but with premixed flames the effect was reversed with respect to isomeric differences in molecular structure. The data presented in Table VIII illustrate that the straight chain paraffins burn dirtier in premixed flames than their branched chain isomers.

TABLE VIII

COMBUSTION CLEANLINESS OF PREMIXED FLAMES

<u>Hydrocarbon</u>	<u>Air Required to Suppress Luminosity, % Stoichiometric</u>
Normal Octane	72
Isooctane	69
Toluene	75
Tetralin	95

3. Aircraft Gas Turbine Type Combustors

Performance requirements of aircraft gas turbine engines have necessitated the design of small combustion chambers capable of burning fuel efficiently over a wide range of operating conditions. In addition, combustion products must be diluted with excess air to uniformly lower temperature before they are fed in continuous flow to the turbine. The flame is usually maintained by a spray of fuel entering the upstream end of the combustor into which air is gradually fed along the full length of the combustor. Ideally, a fuel-air mixture near stoichiometric would be formed, and burned, in a primary combustion zone, followed by a secondary dilution zone. Actually, this is never achieved. Pockets of over-rich fuel-air mixture in the primary combustion zone, and flames quenched before

combustion reactions are complete in the secondary dilution zone, may result in excessive soot formation.

The resulting configurations of combustors for aircraft gas turbine engines are characterized by turbulent diffusion combustion processes, having features of both diffusion and premixed flames. They may favor one or the other, depending upon combustor design and operating conditions. Generally, the effect of isomeric differences in molecular structure on the combustion cleanliness of the hydrocarbon fuels is intermediate.

This is illustrated by the combustion cleanliness characteristic of normal and branched-chain paraffins, relative to an aromatic hydrocarbon, in two quite different laboratory-scale combustors. Small-scale combustors, which are used because of the high cost of test facilities and fuels, have shown excellent correlation with aircraft gas turbine combustor performance in fuel evaluation studies. This is shown by similar data obtained by Naval Air Material Center, Aeronautical Engine Laboratory, using two different full-scale combustors. These data confirm that isomeric differences in hydrocarbon structures have a negligible effect on combustion cleanliness.

Phillips Microburner data, reported by Streets (30) show the effect of fuel type on flame radiation. This index of soot particle concentration in the flame is considered to be the most basic measurement of combustion cleanliness available. Other performance parameters, such as exhaust smoke density, combustor coke deposits, liner temperature, or metal loss, are further complicated by variables in combustor design. The Microburner simulates the primary combustion zone of an aircraft gas turbine combustor, burner pressure was 1 atmosphere, inlet air temperature was 500 F, inlet air reference velocity was 30 feet per second, and fuel-air ratio was 0.070 (approximately stoichiometric). All of the test fuels burned with luminous flames under these operating conditions.

Phillips 2-Inch Combustor data, reported by Miller, Blake, Schirmer, Kittredge, and Fromm (31), show the effect of fuel type on flame radiation, liner temperatures and metal loss, coke deposits, and exhaust smoke. The data in Table IX were obtained at a combustor pressure of 5 atmospheres, inlet air temperature of 400 F, inlet air velocity of 100 ft. per second, and fuel-air ratio at 0.010. The paraffin hydrocarbons burned with partially luminous flames, but toluene flames were brilliantly luminous. The difference in combustion cleanliness between normal heptane and isooctane is negligible when compared with toluene.

TABLE IX
COMBUSTION CLEANLINESS OF LABORATORY COMBUSTOR FLAMES

<u>Hydrocarbon</u>	<u>Phillips Microburner Flame Radiation, Btu/ft²/hr.</u>	<u>Phillips 2-Inch Combustor</u>				
		<u>Average Transverse Flame Radiation, Btu/ft²/hr.</u>	<u>Average Liner Temp., F</u>	<u>Liner Metal Loss, g/hr.</u>	<u>Coke Deposit, g/hr.</u>	<u>Exhaust Smoke Density, % Black</u>
Normal Heptane	27,500	17,000	791	0.32	0.27	1
Isooctane	25,200	15,000	786	0.12	0.10	2
Toluene	63,700	58,000	935	1.19	4.86	15

It has been amply demonstrated that increased operating pressure favors the formation of soot in combustor flames. Higher pressures decrease diffusion coefficients, and may decrease the rate of mixing fuel and air to accentuate diffusion flame processes. More likely, higher pressures increase the rate of soot forming reactions relatively faster than competing oxidation reactions. Data reported by Kittredge (32) indicate that operating pressures to 15 atmospheres in Phillips 2-Inch Combustor did not alter the relative insensitivity of soot forming reactions to isomeric differences in hydrocarbon structure. The combustor was operated at an inlet air temperature of 400 F, inlet air reference velocity of 100 ft./sec., and at heat input rates of 150, 200, 250, and 300 Btu/lb. of air. The data in Table X are

average values over this range of heat input rates. No coke deposits accumulated in the combustor when operating at these high metal temperatures. All the fuels burned with brilliantly luminous flames. The marked reduction in flame radiation flux at the downstream location for toluene results from reabsorption of radiant energy by the quenched exhaust products, which are very high in soot content. The difference in combustion cleanliness between normal heptane and isooctane is small when compared with toluene.

TABLE X

COMBUSTION CLEANLINESS OF HIGH PRESSURE LABORATORY COMBUSTOR FLAMES

Phillips 2-Inch Combustor

<u>Hydrocarbon</u>	<u>Transverse Flame Radiation, Btu/ft²/hr</u>	<u>Liner Temp., F</u>	<u>Heat Flux to Liner by Radiation, %</u>	<u>Liner Metal Loss, g/hr.</u>	<u>Downstream Flame Radiation, Btu/ft²/hr</u>	<u>Exhaust Smoke Density, % Black</u>
Normal Heptane	116,000	1610	46	0.85	121,000	32
Isooctane	128,000	1690	47	1.21	99,000	52
Toluene	220,000	1870	70	4.32	97,000	56

Pratt and Whitney J-57 aircraft gas turbine combustor data reported by Schirmer, McReynolds, Daley (33) show the effect of fuel type on flame radiation and liner temperature. Comparable data from a General Electric J-79 aircraft gas turbine combustor are reported by Schirmer (34). Combustor inlet conditions simulated cruise at altitude; combustor pressure was 5 atmospheres, inlet air temperature was 540 F, and heat input rates were 195, 240, and 285 Btu/lb. of air. The data in Table XI are average values over this range of heat input rates. The difference in combustion cleanliness between normalheptane and isooctane is negligible when compared with tetralin.

TABLE XI
COMBUSTION CLEANLINESS OF AIRCRAFT GAS TURBINE COMBUSTOR FLAMES

<u>Hydrocarbon</u>	<u>P & W J-57 Combustor</u>		<u>GE J-79 Combustor</u>	
	<u>Average</u> <u>Transverse</u> <u>Flame</u> <u>Radiation,</u> <u>Btu/ft²/hr.</u>	<u>Average</u> <u>Liner</u> <u>Temp.,</u> <u>F</u>	<u>Transverse</u> <u>Flame</u> <u>Radiation,</u> <u>Btu/ft²/hr.</u>	<u>Average</u> <u>Liner</u> <u>Temp.,</u> <u>F</u>
Normal Heptane	48,000	723	50,000	825
Isooctane	67,000	765	53,000	812
Tetralin	177,000	995	114,000	1070

It has been shown by illustration that the combustion processes and the diffusion flames and premixed flames are quite different. Diffusion flames are cleanest with normal paraffin hydrocarbons, while premixed flames are cleanest with isoparaffin hydrocarbons. However, there is no distinguishable difference between normal paraffin and isoparaffin hydrocarbons in the cleanliness of turbulent diffusion flames, such as exist in aircraft gas turbine combustors.

B. Mechanism of Soot Formation

The mechanism of soot formation during the combustion of hydrocarbons has interested chemists for over a century. In describing Sir Humphry Davy's researches on flames, 1815 to 1819, which led to his invention of the Miners' Safety Lamp, Bone and Townend (28) report that Davy was the first to realize that: (a) brilliant and dense (luminous) flames result from the presence of incandescent solid matter, (b) solid carbonaceous material (soot) can be produced by decomposition of fuel in an oxygen deficient portion of a hydrocarbon-air flame. However, the identification of soot as the cause of flame luminosity leaves the decomposition of hydrocarbon molecules to soot particles unexplained. An understanding of the mechanism of soot formation in flame may elucidate the differences observed in combustion cleanliness between diffusion flames and premixed flames.

A particle of soot contains upward of 50,000 carbon atoms, with about one atom of hydrogen for every ten atoms of carbon. The hydrogen is believed to be a remnant of the original hydrocarbon molecule. Formation of a particle of soot from small hydrocarbon molecules must obviously have involved both condensation and dehydrogenation reactions. Theories on the mechanism of soot formation differ mainly in the route by which these two essential changes take place. Gaydon and Wolfhard (34) have presented an up-to-date authoritative review of theories on the mechanism of soot formation in flames. The abundance of theories may in part result from real differences in the detailed mechanism of soot formation with variations in both the conditions in the flame and the molecular structure of the fuel.

In diffusion flames the complete conversion of several fuel molecules into soot particles must take place within about ten milliseconds. In premixed flames only about one millisecond is available. Thomas (35) points out that such short times require extremely fast reactions, indicating that the growing intermediates in the process of soot formation are highly conjugated free radicals. A soot particle is pictured as a very large polybenzenoid free radical, formed by condensation of conjugated polyene radicals or aromatic radicals, produced by dehydrogenation of the parent fuel molecule. This concept allows us to examine the initial reactions in diffusion flames and premixed flames for an explanation of the variation in sooting tendency of normal paraffins and their isomers.

1. Reactions in Diffusion Flames

Wolfhard and Parker (36) have shown that molecular oxygen does not penetrate the hydrocarbon core of a diffusion flame. Therefore, we can assume that thermal decomposition of a hydrocarbon molecule will follow the free-radical theory of cracking, as modified by Kossiakoff and

Rice (37). They postulate a radical chain process based on the removal of hydrogen atoms from paraffin molecules by small alkyl radicals, leaving large radicals that decompose rapidly in a definite way and ultimately regenerate small radicals to continue the chain. Detailed analytical data by Voge and Good (38) confirm that: (a) the long straight chain normal paraffin molecules generally undergo carbon-to-carbon bond scission, with cleavage of stable low molecular weight products, such as methane, ethane, and ethylene, (b) the highly branched chain isoparaffin molecules suffer substantial dehydrogenation and yield large quantities of relatively unstable high molecular weight olefins, such as butylene.

Further attack in the flame on products obtained from thermal cracking of isoparaffins could readily lead to the conjugated polyene radicals capable of rapidly condensing to the polybenzenoid structure of soot. The greater combustion cleanliness of normal paraffins over isoparaffins in diffusion flames is to be expected from knowledge of hydrocarbon pyrolysis.

2. Reactions in Premixed Flames

Having conveniently considered the purely thermal process of hydrocarbon decomposition first, we are now in position to inquire about the difference introduced by the presence of oxygen. Pease (39) reviewed data showing that oxygen greatly accelerates the rate of hydrocarbon degradation, and that the initial attack by oxygen under these conditions involves selective dehydrogenation of the hydrocarbon molecule. Therefore, we can expect an acceleration in the rate of formation of conjugated polyene radicals. However, a rapid and sustained attack by oxygen, if available, can consume the carbon skeleton of such particles before competing condensation reactions produce soot.

Lewis and von Elbe (40) have pointed out that hydrogen stripping by effective collisions between oxygen molecules or free radicals with the long straight chain paraffins is much easier than with the compact molecules of isoparaffins. The difference in reactivity between normal paraffins and isoparaffins is thoroughly documented and the consequences are well known from their effect on the fuel requirements of Otto-cycle engines. Isoparaffins have more time to undergo cracking reactions with cleavage of metal and alkyl radicals.

Street and Thomas (29) reasoned that the critical concentration of oxygen required to suppress soot formation in a premixed flame is not reached until the remaining hydrocarbon fragments can no longer react as in a diffusion flame to produce soot. They suggested that this critical concentration is a function of the uniformity of oxygen distribution over all carbon atoms. Oxygen is most effectively utilized by modes of attack that promote hydrocarbon decomposition to oxidized fragments. The structure of the fuel molecule governs the fashion in which oxidation proceeds: (a) isoparaffins favor fragmentation, which allows for effective distribution of the oxygen over all the carbon atoms early in the reaction sequence, (b) normal paraffins undergo unhindered dehydrogenation, which squanders liberal amounts of oxygen and leaves large reactive hydrocarbon fragments.

These concepts of hydrocarbon decomposition in premixed flames are a complete reversal from those outlined in diffusion flames. In premixed flames fragmentation is favored for the isoparaffins and dehydrogenation for the normal paraffins, while in diffusion flames the opposite occurs. Performance data with pure hydrocarbons support these concepts. Furthermore, these concepts seem quite tenable with the intermediate performance observed in aircraft gas turbine type combustors, where isomeric differences in hydrocarbon structure have a negligible effect on combustion cleanliness.

C. Jet Fuel Hydrogen Content

The hydrogen content of a pure hydrocarbon, or of a complex mixture of hydrocarbons such as in a normal jet fuel, is a basic property of the specific fuel sample and can be determined with considerable accuracy by a variety of techniques. It has long been realized that the hydrogen content of a jet fuel has direct bearing on its combustion cleanliness characteristics. The logic of its specification for control of burning quality has immediate appeal. However, preoccupation with combustor coke deposits in the past has promoted correlation factors that included corrections for variations in fuel volatility. Improvements in combustor design and an increasing awareness of the whole combustion cleanliness problem makes the simple use of hydrogen content alone appear feasible now.

1. Relationship to Combustion Cleanliness

The effect of fuel properties on combustion-chamber coke deposition was investigated by Jonash, Wear, and Cook (41). Twenty JP-3 and JP-4 type jet fuels were evaluated in an Allison J-33 turbojet engine combustor. Correlations with coke deposits were attempted using three empirical fuel factors:

- (a) Smoke Point (16)
- (b) Smoke-Volatility Index; a function of Smoke Point and distillation characteristics of the fuel, defined as:

$$\text{SVI} = \text{Smoke Point} + 0.42 (\text{volume per cent fuel boiling under 400 F}).$$

- (c) NACA K Factor; a function of volumetric average boiling temperature (°F) and hydrogen-carbon ratio of the fuel, defined as:

$$K = (\text{°F} + 600) (0.7) \frac{(\text{H/C}) - 0.207}{(\text{H/C}) - 0.259}$$

Limitations on Smoke Point and Smoke-Volatility Index are currently used

in some jet fuel specifications for control of combustion cleanliness. A comparison of the relative precision of these three fuel factors was made using deviations of deposit data from correlation curves. The coke deposit data are averages of from 2 to 5 test runs for a given fuel; average deviations of test results for a given fuel varied from 1 to 16 per cent, with a mean of 6 per cent. This same deposit data has been used in the present study to develop the correlation with hydrogen content. Figure 17 shows a comparison of correlations of hydrogen content or Smoke Volatility Index with coke deposits. The comparison of all four fuel-factors is presented in Table XII.

TABLE XII

DEVIATION OF J-33 COMBUSTOR DEPOSIT DATA FROM CORRELATION CURVES

<u>Fuel-Factor</u>	<u>Average Deviation, %</u>	<u>Maximum Deviation, %</u>
Smoke-Volatility Index	27	95
Smoke Point	17	67
Hydrogen Content	17	48
NACA K Factor	12	30

Best correlations were obtained using NACA K factor and hydrogen content. It should be noted that the NACA K factor was empirically developed specifically for correlation with combustor coke deposition. In effect, it is fuel hydrogen content corrected for fuel volatility to compensate for design limitations in early turbojet combustors.

A more recent study by Macaulay and Shayeson (42) is significant because it specifically proposes utilization of the hydrogen content of a hydrocarbon fuel as an index of its burning quality. Measurements of (a) combustor liner metal temperature, (b) flame radiation intensity, (c) exhaust gas soot content, and (d) combustor coke deposition were made using a General

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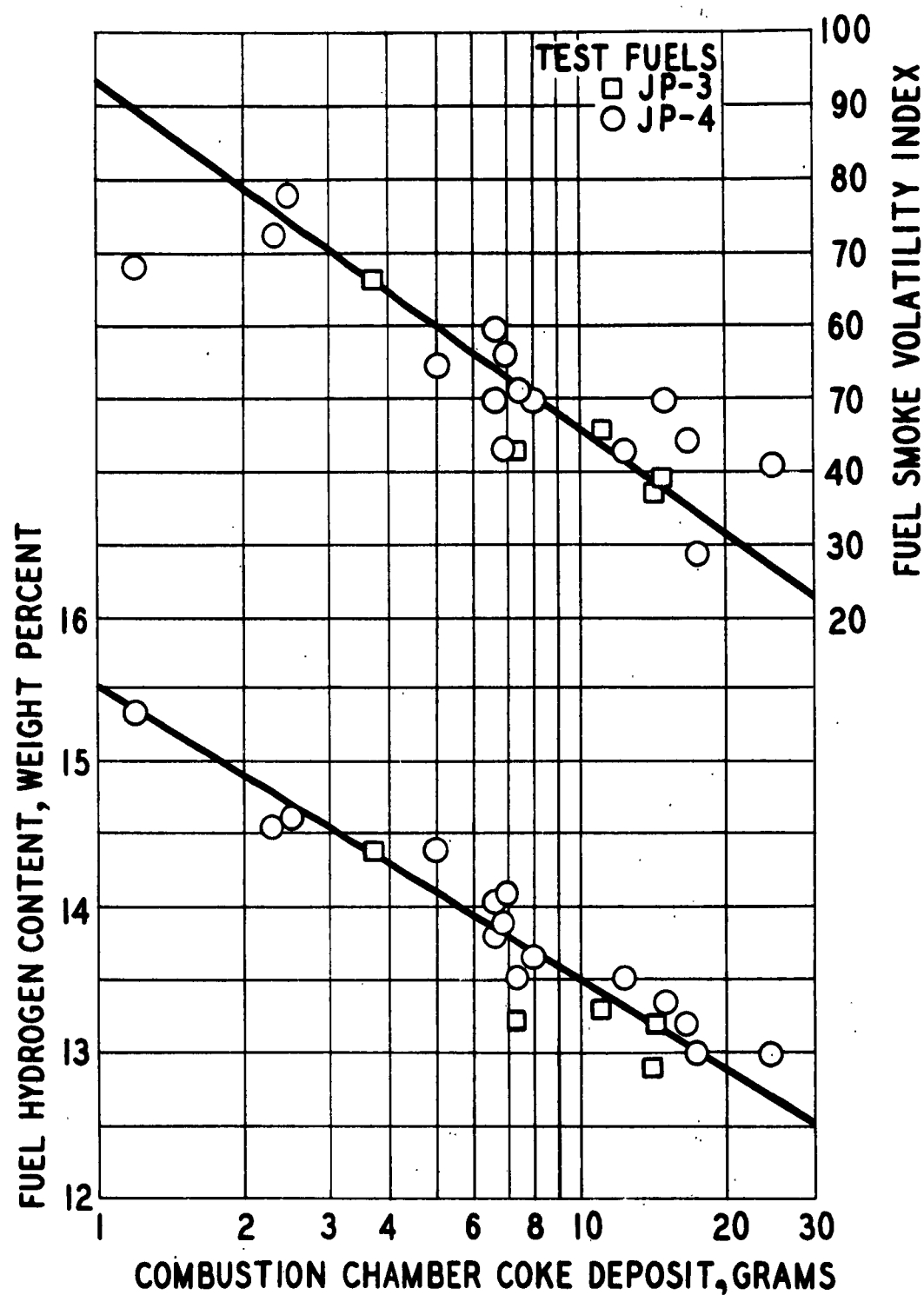


FIGURE 17
COMPARISON OF CORRELATIONS FOR AN
ALLISON J-33 TURBOJET ENGINE COMBUSTOR
AT ALTITUDE CRUISE CONDITIONS

Electric CJ-805 turbojet engine combustor. Some 27 different fuels were tested, varying from JP-4 through diesel fuel. Improved design of combustors in modern aircraft gas turbine engines limits coke deposition. This leaves the more difficult combustion cleanliness problems of soot formation in the flame, which contributes by radiation to liner temperature. A change of 400 F in average liner temperature occurred in this combustor as a direct result of variations in fuel properties. Comparison of the relative precision of three fuel-factors was made by correlation curves with average liner temperature. Two of these correlation curves, hydrogen content and Luminometer Number versus liner temperature, are shown in Figure 18 for visual comparison. Deviations of the liner temperature data from these correlation curves have been calculated during the present study for all three fuel-factors. These are shown in Table XIII.

TABLE XIII

DEVIATION OF CJ-805 COMBUSTOR LINER TEMPERATURE DATA

FROM CORRELATION CURVES

<u>Fuel-Factor</u>	<u>Average Deviation, %</u>	<u>Maximum Deviation, %</u>
Smoke Point	3.2	9.9
Luminometer Number	3.5	10.3
Hydrogen Content	2.1	9.0

Smoke Point (16) and Luminometer Number (17) are currently used in some jet fuel specifications for control of combustion cleanliness. The best correlation was obtained using fuel hydrogen content.

The Pratt-Whitney J-57 aircraft gas turbine combustor data previously referenced (33) are of further interest because measurements of both liner temperature and flame radiation are reported for a dozen different test fuels of known hydrogen content. The first five of these

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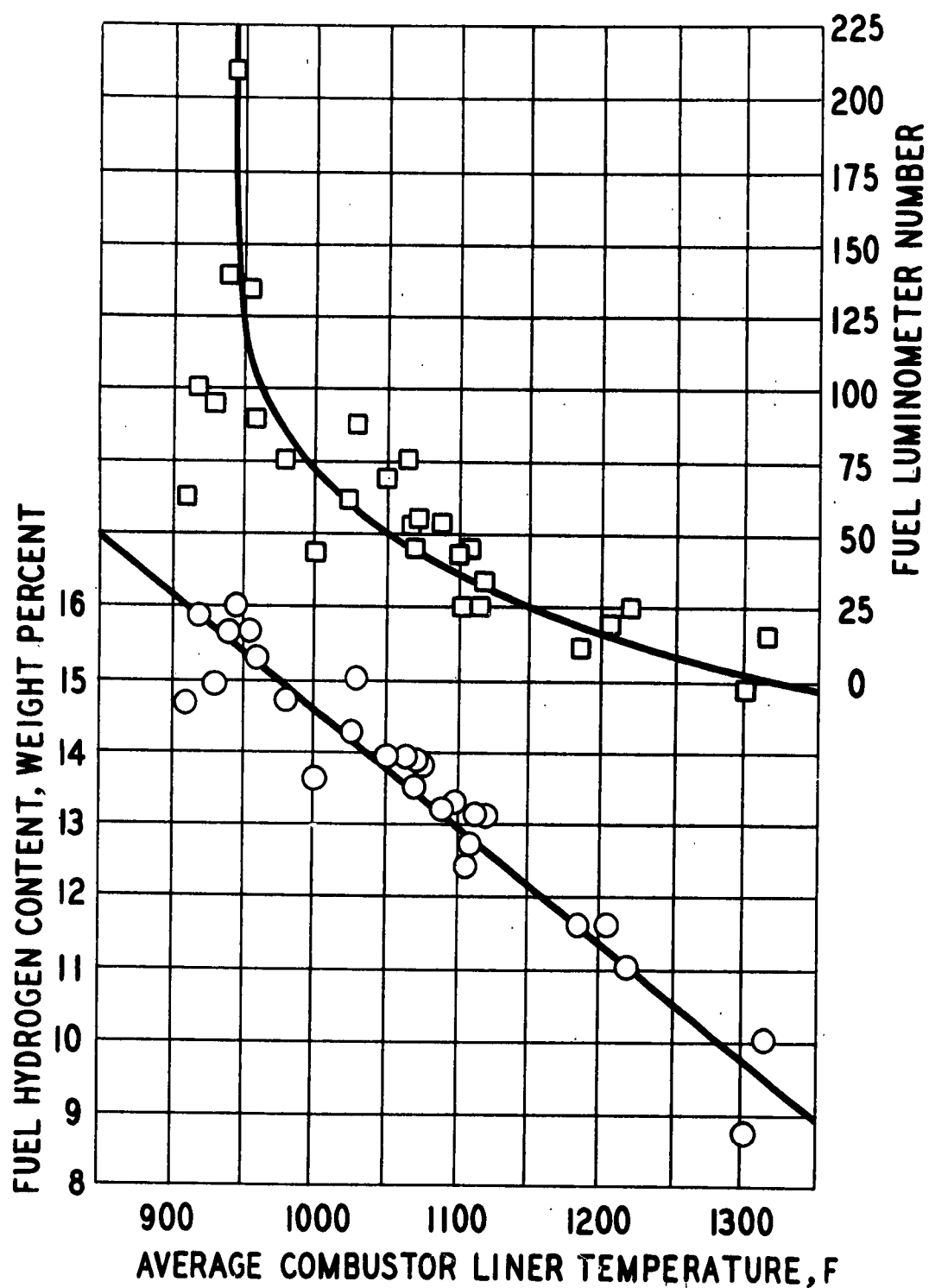


FIGURE 18
COMPARISON OF CORRELATIONS FOR A
GENERAL ELECTRIC CJ-805 TURBOJET ENGINE COMBUSTOR
AT ALTITUDE CRUISE CONDITIONS

test fuels were blended specifically to allow evaluation of the relative effects of monocyclic versus polycyclic aromatics on the combustion cleanliness of JP-5 type jet fuels. A brief description of all of these test fuels is presented in Table XIV. The hydrogen contents of these fuels were determined by semi-micro analysis with exceptions indicated.

TABLE XIV
TEST FUELS USED IN J-57 COMBUSTION CLEANLINESS STUDY

Test Fuel No.	Description	Hydrogen Content, %	Luminometer Number
1	Aromatic Free JP-5	14.4	70
2	No. 1 Plus 6.5% Monocyclic Aromatics	14.2	59
3	No. 1 Plus 17.3% Monocyclic Aromatics	13.9	46
4	No. 1 Plus 3.8% Polycyclic Aromatics	14.0	58
5	No. 1 Plus 9.6% Polycyclic Aromatics	13.5	42
6	Mixed Alkyl Decalins	13.5	47
7	Low Luminosity Kerosine (JP-150)	15.7 (a)	136
8	Production JP-4	14.1	67
9	Production JP-5	13.7	47
10	Isooctane	15.9 (b)	100
11	Normal Heptane	16.1 (b)	181
12	Tetralin	9.2 (b)	-1

Notes: (a) Calculated assuming nonane.

(b) Calculated assuming a pure hydrocarbon.

These data have been used in Figure 19 to compare correlations between hydrogen content or Luminometer Number versus liner temperature. Similarly, correlations of these same two fuel-factors with the more fundamental combustion cleanliness parameter of flame radiation are presented in Figure 20. While it was felt that insufficient data points were available

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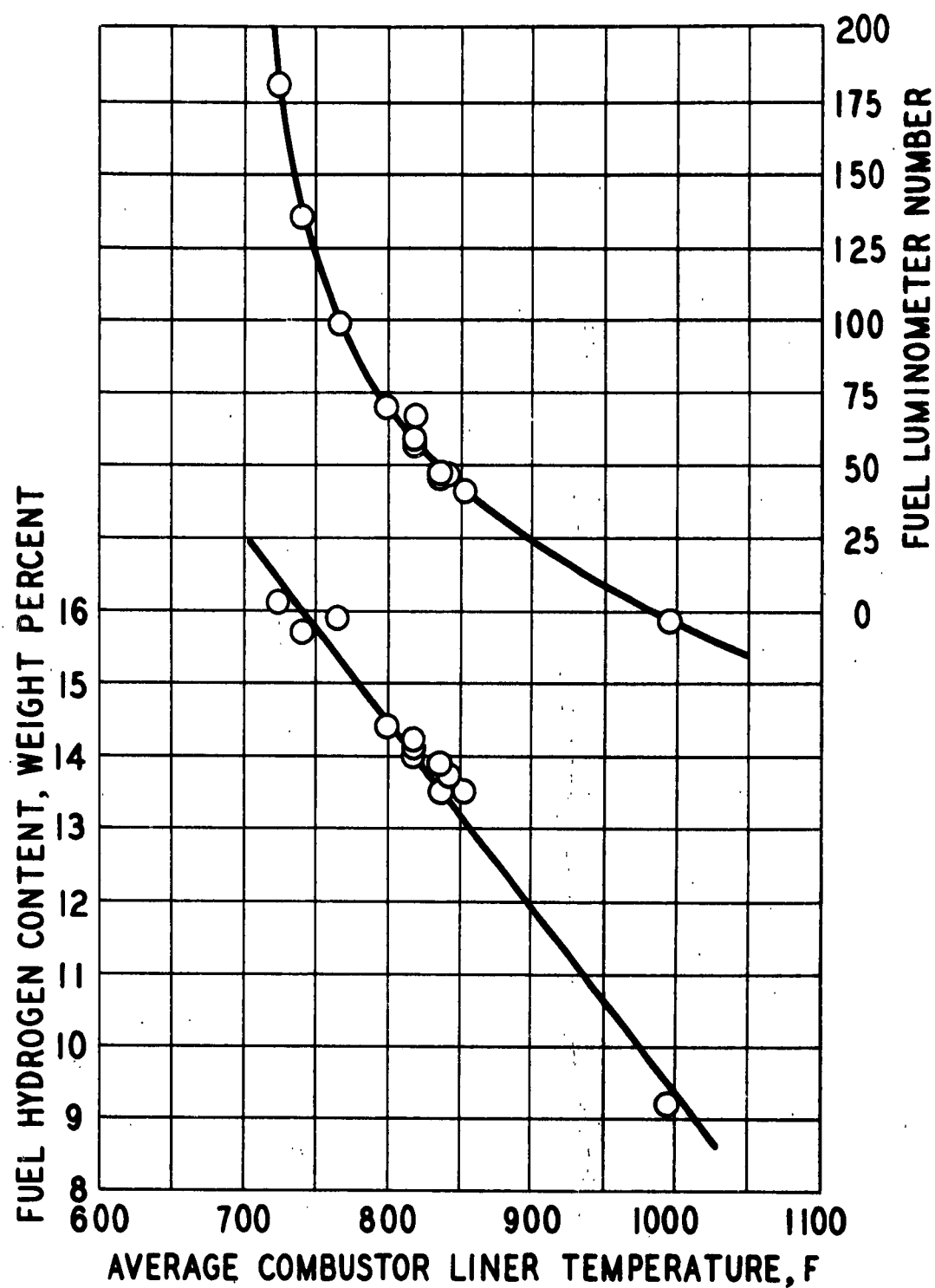


FIGURE 19
COMPARISON OF CORRELATIONS FOR A
PRATT & WHITNEY J-57 TURBOJET ENGINE COMBUSTOR
AT ALTITUDE CRUISE CONDITIONS

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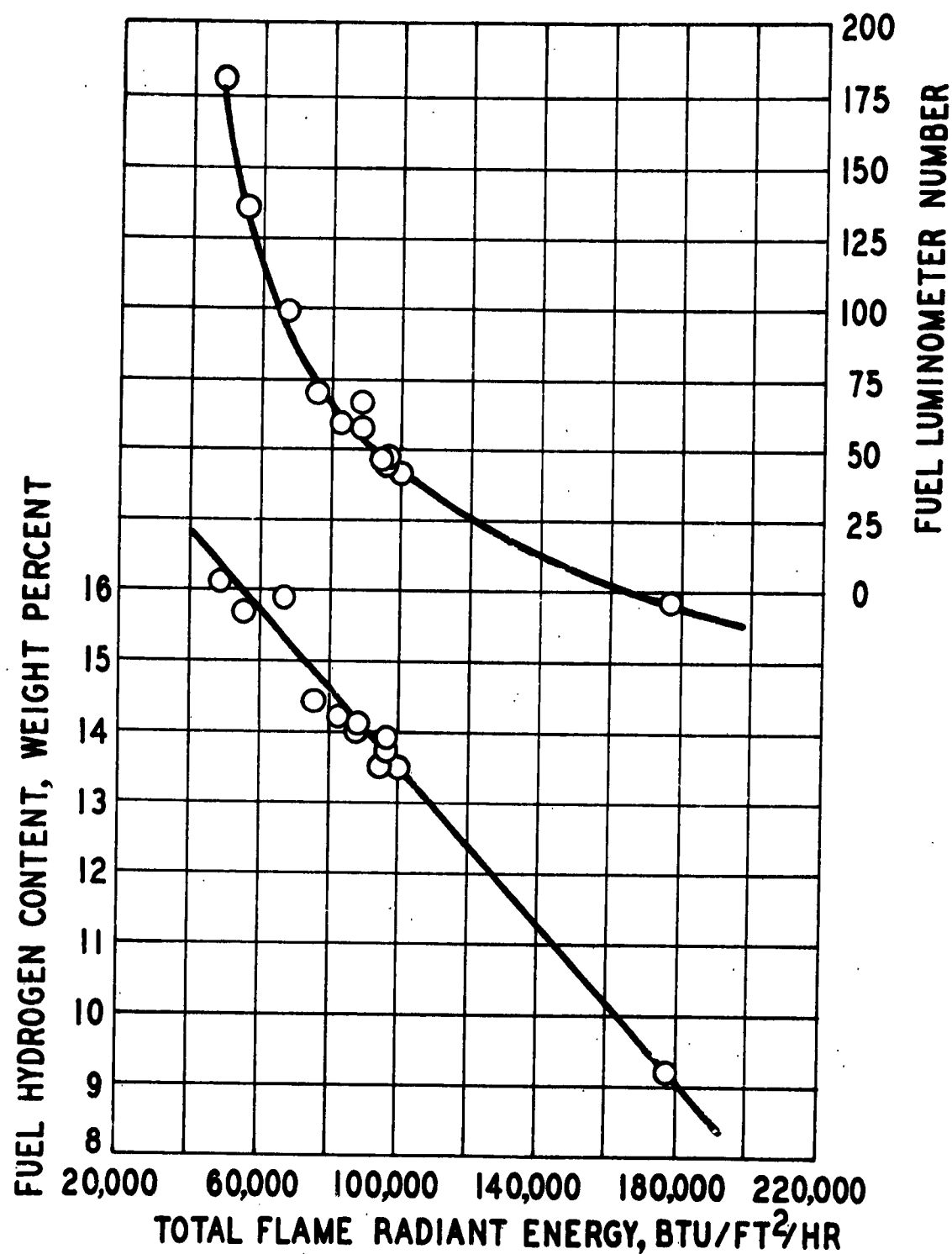


FIGURE 20
COMPARISON OF CORRELATIONS FOR A
PRATT & WHITNEY J-57 TURBOJET ENGINE COMBUSTOR
AT ALTITUDE CRUISE CONDITIONS

to calculate a significant average deviation from these correlation curves, the excellence of those made by the use of fuel hydrogen content is obvious in both cases.

Phillips 2-Inch Combustor data have been obtained by Kittredge (43) using the fuels described in Table XIV. As with the J-57 combustor, operating pressure was at 5 atmospheres. These data are plotted in Figure 21 to compare correlations between hydrogen content or Luminometer Number versus flame radiation. The correlations between combustion cleanliness and hydrogen content in all of these combustors are straight lines. This characteristic is highly desirable for it prevents undue emphasis being placed on a fuel quality, such as a very high Luminometer Number, from which no actual benefit in terms of aircraft gas turbine engine performance or durability can reasonably be expected.

2. Determination

Lavoisier's classic investigation of the process of combustion (1772 to 1777) produced the first crude technique for quantitative organic analysis (44). The organic substance was burned in a small lamp floating on mercury in a bell jar containing oxygen. Carbon dioxide was measured by absorption in potassium hydroxide solution. While this technique established that carbon and hydrogen were always present in organic substances, it was not sufficiently accurate for determination of their relative proportions.

A precise technique for quantitative organic analysis was not achieved until a half century later (1831) by Liebig (45). In principle, it is still used today. A weighed amount of sample is heated by a furnace in a metered stream of oxygen, the tube is packed with copper oxide to insure complete combustion. The combustion gases are passed over a tube filling that removes interfering substances. The resulting carbon dioxide and water are absorbed under conditions that enable their separation. The carbon and hydrogen contents are usually calculated from the increase in weight of the absorbents.

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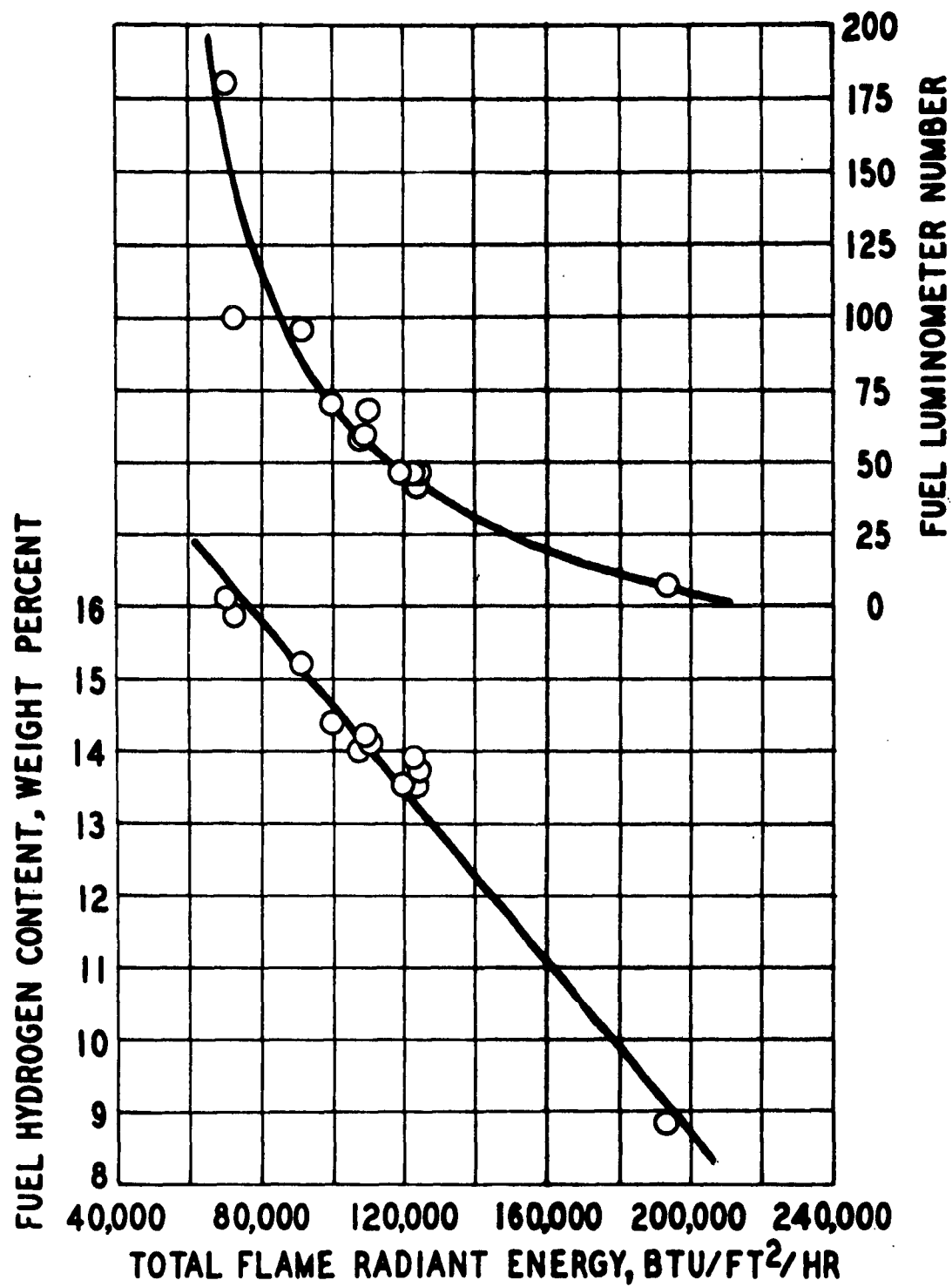


FIGURE 21
COMPARISON OF CORRELATIONS FOR A
PHILLIPS 2-INCH COMBUSTOR
AT 5 ATMOSPHERES PRESSURE

Improvements in materials during the following century gradually reduced the quantity of sample required for the classical Liebig method to about 100 milligrams. In 1910, Pregl reduced the required sample size to about 5 milligrams by use of a microbalance and special manipulative techniques (46). Pregl's method for determination of carbon and hydrogen is regarded as the classical procedure of microchemical analysis and is more widely used than any other. Variations in procedure to simplify technique and minimize errors are legion; the work of Niederl and Niederl (47) is an outstanding example. Petroleum chemists often use a less elaborate compromise method requiring about a 15 milligram sample, which is known as semimicro and described by Clark (48). Scott, Puckett, Price, Grimes and Heinrich (49) have developed an interesting modification, called the semimicro manometric method, in which the combustion produced water and carbon dioxide are separated cryogenically and their volumes measured directly.

It is important to the research chemist working on manufacturing processes to have a method of test for specification of the combustion cleanliness characteristics of jet fuels that requires a small sample. In addition, sample size is important from the safety standpoint in rapid oxidation procedures; this is the significant factor in the preference by analytical chemists for the micro and semimicro methods for organic analysis.

It is unnecessary to specify both hydrogen and carbon content of present aircraft gas turbine fuels for control of combustion cleanliness. The content of elements other than hydrogen and carbon is negligible. The method is simplified if only hydrogen content of the fuel need be specified. Therefore, determination of both hydrogen and carbon content of the fuel serves no purpose unless done to establish the hydrogen-carbon ratio and thereby avoid the initial sample weighing.

Microanalytical equipment is delicate and manipulative techniques are demanding. To reduce the requirements of operator skill a completely automatic combustion apparatus has been developed for hydrogen analysis by Coleman (50). On the other hand, the test method for hydrogen in petroleum fractions adopted by ASTM (51) has simplified equipment by reverting to a wick lamp such as Lavoisier used.

The recent instrumental approach to quantitative organic analysis seems to offer the possibility for even further reduction in sample size. Duswalt and Brandt (52) have demonstrated that the combustion produced water can be converted to acetylene by inclusion of a calcium carbide tube in the tray; acetylene can be determined by quantitative gas chromatography. Sundberg and Maresh (53) claim that this allows a reduction in sample size to 1.5 milligrams, with potential reduction to the deci-milligram level. Similarly, the combustion-produced water vapor can be determined by the quantitative electrolysis technique of Keidel (54), which has allowed Haber and Gardiner (55) to reduce sample size to one milligram, or less. Finally, Gray, Clarey, and Beamer (56) have developed an analytical method for hydrogen using beta-ray back-scattering, which is non-destructive and thus consumes no sample.

A quick test method is also desirable for promoting the progress of research as well as avoiding a refinery control bottle neck. The new instrumental methods offer a substantial reduction in time required for determination of hydrogen in jet fuel, as shown in Table XV. Some of them, such as beta-ray absorption proposed by Berthold (57) also offer the possibility of continuous analysis for automatic product monitoring and refinery control.

TABLE XV

TIME REQUIRED FOR DETERMINATION OF HYDROGEN CONTENT

<u>Test Method</u>	<u>Total Analysis Time, Minutes</u>
Pregl Microanalysis	135
Lamp Hydrogen Macroanalysis	120
Semimicro Gravimetric Procedure	60
Semimicro Manometric Procedure	30
Automatic Hydrogen Microanalyzer	30
Gas Chromatography Microanalysis	20
Water Electrolysis Microanalysis	10
Beta-Ray Back-Scattering	5

3. Accuracy

The term accuracy is used by the analytical chemist to denote conformity between the measured result and the "true value" of composition. The accuracy of hydrogen determination is a matter of considerable importance in organic chemistry. The Liebig macro combustion method made it possible for an analyst to work within ± 0.3 percentage points of the theoretical hydrogen content of a substance (45). This degree of accuracy is accomplished in part by the use of a sufficiently large sample to offset error. Pregl's micro method made it possible to greatly reduce the size of samples while maintaining this degree of accuracy (47). The micro method was duly recognized as one of the achievements of modern science by the award to Pregl of the Nobel Prize in 1923. It should be noted that accuracy has been improved up to an order of magnitude by use of larger size samples with micro techniques (46). This approach has made possible an accuracy of ± 0.1 per cent for hydrogen with a semimicro procedure (48), and the ASTM Lamp Hydrogen Method (51). No further improvements in accuracy have been conclusively demonstrated by application of instrumental techniques.

The term precision is taken to mean the consistency of the obtained results among themselves. It is of necessity applied to performance tests where the results are a function of test equipment design. The precision of a performance test is usually established at a 95 per cent probability level for both repeatability (same operator and apparatus) and reproducibility (different operator and apparatus). Such data are available for the ASTM test methods of interest for control of combustion cleanliness, as shown in Table XVI.

TABLE XVI

PRECISION OF ASTM TEST METHODS

<u>Test Method</u>	<u>Repeatability</u>	<u>Reproducibility</u>
Luminometer Number (17), 0 to 150	6.2	9.3
Smoke Point (16), up to 20 mm	1	2
20 to 30 mm	1	3
30 to 40 mm	1	4
Hydrogen Content (51), 11 to 16 Wt. %	0.11	0.18

These data are difficult to compare in the form given, so precision has been recalculated as percentage of the difference between isooctane and toluene, the Smoke Point Method reference fuels. The comparison is made in Table XVII. Similar results are obtained if precision is calculated as percentage of the difference between isooctane and tetralin, Luminometer Method reference fuels.

TABLE XVII

COMPARATIVE PRECISION OF ASTM TEST METHODS

<u>Test Method</u>	<u>Performance Range, Isooctane - Toluene</u>	<u>Repeatability</u>	<u>Reproducibility</u>
Luminometer Number	100 - 5 = 95 LN	6.5%	9.8%
Smoke Point	40 - 8 = 32 mm	3.1%	9.4%
Hydrogen Content	15.9 - 8.8 = 7.1 Wt. %	1.5%	2.5%

The use of hydrogen content for control of jet fuel combustion cleanliness would afford a two-to-fourfold improvement in repeatability and a fourfold improvement in reproducibility over current test methods.

The precision of specification test methods is important to all concerned, for without the assurance that subsequent quality checks will accept the product, excess quality must be provided, at additional cost. Additional advantages are offered by the accuracy of test methods measuring a fundamental fuel variable, such as hydrogen content. For example, a research chemist might select a semimicro combustion method for complete quantitative organic analysis in studying new petroleum processing techniques. A process engineer might choose the beta-ray back-scattering method to obtain continuous monitoring of product quality for automatic refinery control, while the product inspector might prefer a portable method, using a micro-syringe to measure the sample, with direct readout of hydrogen content from an electrolytic cell.

IV. CONCLUSIONS

An evaluation of the effect of fuel sulfur contamination on the loss of metal from simulated turbine inlet guide vanes operating at 2000 F has been conducted using the Phillips 2-Inch Research Combustor operating under conditions typical of take-off and low altitude cruise for a 12:1 compression ratio turbojet. Five typical current-generation superalloys were tested. The results indicate the following:

1. Guide vane metal loss is approximately a linear function of exposure time regardless of fuel sulfur content.
2. Conventional evaluation of the data indicates that the addition of 1.0 percent sulfur to the isoparaffinic base fuel had either no effect or an apparent beneficial effect on the durability of this group of alloys. Analysis using statistical methods indicates that the sulfur had no effect on metal durability.
3. With regard to the relative durability of the five alloys, Haynes Alloy 25 lost the least metal, Hastelloy R-235 the most during the 12 hours total test duration. These extremes differed by a factor of about four while Udimet 500, Waspalloy and René 41 were comparable and intermediate in performance.

Tensile strength tests conducted on the simulated turbine inlet guide vane specimens before and after exposure to sulfur-free and sulfurous exhaust gases at 2000 F in the Phillips 2-Inch Research Combustor have shown the following:

1. Only two of the five alloys tested, Haynes Alloy 25 and Waspalloy, showed more degradation of tensile strength by the addition of 1.0 percent sulfur to the fuel than was observed with sulfur-free fuel.

Haynes Alloy 25 lost nearly twice as much tensile strength with sulfur as without. The indicated degradation of Waspalloy by sulfur is considered only marginally significant.

2. All alloys tested suffered marked losses in ductility following exposure in the combustor. No sulfur effect was indicated.

3. In general, the "after exposure" stress-strain curves followed the "before exposure" curves within the elastic range. This result suggests the formation of intergranular oxides which might alter the strength very little during elastic deformation, but be unable to withstand plastic deformation thus resulting in failure at lower strains and lower stresses.

Microscopic examination of the simulated turbine inlet guide vane specimens before and after exposure in the combustor has indicated that:

1. When attack was detected in the photomicrographs it appeared to be primarily intergranular.
2. Regardless of the mechanism, the photomicrographs generally corroborate the metal loss and tensile strength results in that they also show no greater attack with sulfur in the fuel than without.
3. The photomicrographs also support the metal loss data with respect to the relative performance of the five alloys - Haynes Alloy 25 pictures indicate least attack, Hastelloy R-235 most attack.

A brief feasibility study of the potential usefulness of the Phillips Microburner as a hot gas source to supplement the 2-Inch combustor and eventually provide a means for more rapid evaluation of the effect of fuel and air contaminants on turbine blading alloys was carried on during this contract. The results show that:

1. Correlation of Microburner and Phillips 2-Inch Combustor metal loss data appears encouraging.
2. Microburner tests were limited in order to do more testing in the 2-Inch Combustor, which more nearly simulates actual operational conditions. At some time in the future, however, after a greater volume of metal durability data has been obtained in high pressure combustors, it may become desirable to resume testing with the Microburner in order to establish whether or not a useful correlation exists between this atmospheric combustor and high pressure combustors.

The results of a series of six-hour 2000 F furnace tests on five typical current-generation superalloys, conducted to reproduce a type of corrosion known colloquially as "black plague" and to evaluate the relative importance of the several factors (unburned carbon, ingested sea salts, and/or fuel sulfur contamination) postulated in the literature as responsible for the attack, have shown the following:

1. When appreciable attack of the alloys was observed it fit quite well the descriptions outlined by other investigators, indicating that "black plague" had been reproduced by these means.
2. Metal loss was not always a reliable index to degree of attack. When metal losses were high the visual ratings indicated very severe attack, but the converse was not always true.
3. It would appear desirable in future tests, to employ electrochemical descaling other than rotary wire brush descaling.
4. This series of tests confirms the potentiality of extremely severe attack - in fact, catastrophic failure.
5. On an individual basis only sea salt caused any significant attack relative to the "air only" baseline.

6. The effect of sea salt alone and in combination with carbon and/or sulfur dioxide was found to be specific to certain alloys. René 41 was almost completely destroyed during the air and sea salt run, while Udimet 500 showed only slight to medium attack.

7. The possible detrimental effect of carbon as a postulated reducing agent for protective chromium oxide surface films was confirmed in tests with air + carbon + sulfur dioxide. Although neither carbon nor sulfur dioxide by themselves were detrimental, together they brought about severe to very severe attack of all the alloys.

8. Carbon was found to accelerate sea salt corrosion of Waspalloy, Hastelloy R-235 and Udimet 500 while it markedly inhibited sea salt corrosion of René 41 and Haynes Alloy 25.

9. When sulfur was provided by both sea salts and sulfur dioxide (no carbon) results varied from mild acceleration by the added SO₂ with Udimet 500 to pronounced inhibition with René 41, although the R-41 was still badly corroded.

10. When carbon was included while supplying sulfur in the form of both sulfur dioxide and sea salts, the attack was definitely accelerated except in the case of René 41 where, again, the attack was apparently inhibited.

11. Except for René 41, the combination of air + carbon + sulfur dioxide + sea salt was the most severe condition investigated, the balance of the alloys suffering catastrophic corrosion.

12. Checks for magnetic properties in scale removed from each test strip showed that all were non-magnetic.

13. Checks for magnetic properties in the test strips following furnace exposure showed that a number of them had become strongly magnetic, suggesting enrichment in nickel and/or cobalt by virtue of losses in non-magnetic alloying metals.

A critical analysis was made of the current test methods, Smoke Point and Luminometer Number, for evaluation of the burning quality of hydrocarbon fuels for aircraft gas turbine engines. The ratings of fuels by these methods were correlated with measurements of their cleanliness in full scale aircraft gas turbine combustors. Similar correlations of performance were made with the hydrogen content of these fuels. The results of this analysis indicate that hydrogen content shows a good linear correlation with full-scale combustor radiation data while Smoke Point and Luminometer Number correlations show a greater scatter of points and departure from linearity.

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APPENDIX I

ANALYSIS OF VARIANCE (TWO VARIABLES OF CLASSIFICATION - SINGLE OBSERVATIONS)
OF TWO-INCH COMBUSTOR DATA ON DURABILITY OF SUPERALLOY TURBINE GUIDE VANES

	<u>Sum of Squares</u>	<u>Degrees of Freedom</u>	<u>Mean Square</u>
Metal Means	172.366	4	43.0915
Fuel Means	9.801	1	9.8010
Residual	<u>4.114</u>	<u>4</u>	<u>1.0285</u>
Total	186.281	9	

$$F(\text{metal means}) = \frac{43.0915}{1.0285} = 41.90; F_{.975}(4,4) = 9.60$$

Reject hypothesis of no difference among means of different metals.

$$F(\text{fuel means}) = \frac{9.8010}{1.0285} = 9.53; F_{.975}(1,4) = 12.20$$

Accept hypothesis of no difference among means of different fuels.